TECHNOLOGY DEPT.
PUBLIC LIBRARY
DETROIT

# JOURNAL OF THE CHEMICAL SOCIETY

AUGUST, 1944

***PATRON:***
HIS MAJESTY THE KING

***President:***
W. N. HAWORTH, D.Sc., F.R.S.

***Vice-Presidents***
who have filled the office of President:

F. G. DONNAN, C.B.E., D.Sc., LL.D., F.R.S.
PERCY F. FRANKLAND, C.B.E., D.Sc., LL.D., F.R.S.
W. H. MILLS, M.A., Sc.D., F.R.S.
SIR ROBERT ROBINSON, M.A., D.Sc., LL.D., F.R.S.
N. V. SIDGWICK, C.B.E., D.Sc., LL.D., F.R.S.
W. P. WYNNE, D.Sc., M.A., F.R.S.

***Vice-Presidents:***

E. J. BOWEN, M.A., F.R.S.
F. H. CARR, C.B.E., D.Sc., F.R.I.C.
SIR ALFRED EGERTON, M.A., F.R.S.
A. FINDLAY, M.A., D.Sc., LL.D., F.R.I.C.
C. S. GIBSON, O.B.E., M.A., Sc.D., F.R.S.
C. K. INGOLD, D.Sc., F.R.S., F.R.I.C.

***Treasurer:***
F. P. DUNN, B.Sc., F.R.I.C.

***Secretaries:***
C. W. DAVIES, D.Sc., F.R.I.C.
G. M. BENNETT, M.A., Sc.D., F.R.I.C.
W. WARDLAW, D.Sc., F.R.I.C.

***Ordinary Members of Council:***

M. P. APPLEBEY, M.B.E., M.A., D.Sc.
J. W. BAKER, D.Sc., Ph.D., F.R.I.C.
M. P. BALFE, B.A., Ph.D., F.R.I.C.
J. W. COOK, D.Sc., Ph.D., F.R.S.
H. J. T. ELLINGHAM, B.Sc., Ph.D., F.R.I.C.
F. FAIRBROTHER, D.Sc.
G. S. HARTLEY, D.Sc.
L. HUNTER, D.Sc., Ph.D., F.R.I.C.
D. J. G. IVES, Ph.D., A.R.I.C.
E. R. H. JONES, D.Sc., F.R.I.C.
F. B. KIPPING, M.A., Ph.D.
E. B. MAXTED, D.Sc., Ph.D., F.R.I.C.
R. A. MORTON, D.Sc., Ph.D., F.R.I.C.
E. H. RODD, D.Sc., A.C.G.I., F.R.I.C.
J. D. M. ROSS, M.B.E., M.A., D.Sc.
J. C. SMITH, M.A., M.Sc., Ph.D., D.Sc.
G. B. B. M. SUTHERLAND, M.A., B.Sc., Ph.D.
H. W. THOMPSON, M.A., B.Sc., Ph.D.
W. H. J. VERNON, D.Sc., Ph.D., F.R.I.C.
H. B. WATSON, D.Sc., Ph.D., F.R.I.C.
W. F. K. WYNNE-JONES, D.Sc.

***Ex-Officio Members of Council:***

T. A. HENRY, D.Sc. (*Chairman of the Joint Library Committee*).
L. H. LAMPITT, D.Sc., F.R.I.C. (*Chairman of the Chemical Council and of the Bureau of Chemical and Physiological Abstracts*).
T. S. MOORE, M.A., B.Sc. (*Chairman of the Publication Committee*).

***General Secretary:***
S. E. CARR, F.C.I.S.

***Librarian:***
A. E. CUMMINS.

*Telephone Numbers:* Office, Regent 6322; Library, Regent 1342.

London: THE CHEMICAL SOCIETY, BURLINGTON HOUSE, W.1

# CONTENTS.

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.


PAGE

**General, Physical, and Inorganic.**

101. Molecular Volume and Structure. Parts VII and VIII.
By T. W. GIBLING . . . . . 380

104. The Kinetics of the Reaction between Chlorine and Nitric Oxide.
By ERIC M. STODDART . . . . . 388

**Organic.**

94. The Reduction Potentials of Acridines, with Reference to their Antiseptic Activity.
By B. BREYER, G. S. BUCHANAN, and H. DUEWELL . . . . . 360

95. The Synthesis of Dimethyl Dimethylene *l*-Idosaccharate.
By W. G. M. JONES and L. F. WIGGINS . . . . . 363

96. The Structure of Monomethylene *d*-Glucosaccharolactone.
By W. G. M. JONES and L. F. WIGGINS . . . . . 364

97. Studies on Indene Derivatives. Part III. The Constitution and Some Reactions of Bishydroxyindone. The Photochemical Reduction of Triketohydrindene.
By ALEXANDER SCHÖNBERG and RADWAN MOUBASHER . . . . . 366

98. Azoxysulphones, their Preparation and Properties, with Observations on the Structure of Diazotates.
By W. V. FARRAR and J. MASSON GULLAND . . . . . 368

99. The Reaction between Amines and Unsaturated Compounds containing Halogen attached to one of the Ethylenic Carbon Atoms. Part III. The Influence of a *gem*-Dimethyl Group.
By HARRY C. MURFITT and JOHN C. ROBERTS . . . . . 371

100. The Metal-catalysed Reaction between Acetylene and Hydrogen. Part I. Nickel Catalysts.
By J. SHERIDAN . . . . . 373

102. The Separation of 3-Nitro-1-naphthylamine and 4-Nitro-2-naphthylamine by Maleic Anhydride, and the Monobromination of 4-Nitro-2-naphthylamine.
By HERBERT H. HODGSON and DAVID E. HATHWAY . . . . . 385

103. Photochemical Reactions. Part VIII. Reaction of Ethylenes with Phenanthraquinone.
By ALEXANDER SCHÖNBERG and AHMED MUSTAFA . . . . . 387

105. An Interpretation of the Sandmeyer Reaction. Part V. The Comparative Behaviour of Cuprous, Cupric, and Ferric Chlorides as Catalysts.
By HERBERT H. HODGSON and DOUGLAS D. R. SIBBALD . . . . . 393

106. Evidence for the *iso*Nitrile and Nitrile Structures of Hantzsch's Aryl *syn*- and *anti*-Diazocyanides.
By HERBERT H. HODGSON and EWART MARSDEN . . . . . 395

107. The Preparation and Diazotisation of *p*-Aminomonomethylaniline.
By HERBERT H. HODGSON and EWART MARSDEN . . . . . 398

108. A Method of Nuclear Methylation of Phenolic Substances.
By (MISS) M. G. BARCLAY, A. BURAWOY, and G. H. THOMSON . . . . . 400

109. Steric Inhibition of Resonance. Part I. The Dichloronitrobenzenes.
By GEORGE THOMSON . . . . . 404

110. Steric Inhibition of Resonance. Part II. *m*-Xylidines and *N*-Dimethyl-*m*-xylidines.
By GEORGE THOMSON . . . . . 408

NOTE.—Vitamin-A Aldehyde (Axerophthal).
By E. G. E. HAWKINS and R. F. HUNTER . . . . . 411


# INDEX OF AUTHORS' NAMES.


BARCLAY, (Miss) M. G., Burawoy, A., and Thomson, G. H., 400.
Breyer, B., Buchanan, G. S., and Duewell, H., 360.
Buchanan, G. S. See Breyer, B.
Burawoy, A. See Barclay, (Miss) M. G.
Duewell, H. See Breyer, B.
Farrar, W. V., and Gulland, J. M., 368.
Gibling, T. W., 380.
Gulland, J. M. See Farrar, W. V.
Hathway, D. E. See Hodgson, H. H.
Hawkins, E. G. E., and Hunter, R. F., 411.
Hodgson, H. H., and Hathway, D. E., 385.
Hodgson, H. H., and Marsden, E., 395, 398.
Hodgson, H. H., and Sibbald, D. D. R., 393.
Hunter, R. F. See Hawkins, E. G. E.
Jones, W. G. M., and Wiggins, L. F., 363, 364.
Marsden, E. See Hodgson, H. H.
Moubasher, R. See Schönberg, A.
Murfitt, H. C., and Roberts, J. C., 371.
Mustafa, A. See Schönberg, A.
Roberts, J. C. See Murfitt, H. C.
Schönberg, A., and Moubasher, R., 366.
Schönberg, A., and Mustafa, A., 387.
Sibbald, D. D. R. See Hodgson, H. H.
Sheridan, J., 373.
Stoddart, E. M., 388.
Thomson, G., 404, 408.
Thomson, G. H. See also Barclay, (Miss) M. G.
Wiggins, L. F. See Jones, W. G. M.

***CHINA CLAYS (Kaolin)***
***BALL CLAY (Argile)***
***CORNWALL STONE (China Stone)***
***FELSPAR · KALYTES (Barytes Substitute)***
***ALUMINIUM SILICATE (Talc Substitute)***
***BENTONITE (and British Substitutes)***
***TALC (and British Substitutes)***
***QUARTZ SANDS***
***REFRACTORY CLAYS, BRICKS, TILES, etc. and other products.***

*for use in the manufacture of*

Paper
Textiles
Earthenware
Porcelain
Refractories
Crucibles
Furnace Linings
Furnace Moulds
Insulators
Cement
Stoneware
Glass
Fuses
Paints
Enamels
Rubber Goods
Cables
Ultramarine
Inks
Insecticides
Matches
Fireworks
Medicines
Poultices
Cosmetics
Polishes
Roofing Felts
Soaps
etc.

*THERE ARE MANY TYPES OF CHINA CLAY, BALL CLAY, etc., EACH HAVING ITS OWN PECULIARITIES. THEY DIFFER IN ANALYSES, PARTICLE SIZE, COLOUR, SUSPENSION, etc. They can be supplied in bulk or in finest powder form.*

- ***Let us know what you are seeking***

*and we will make recommendations and supply copious samples for tests.*

*Our British substitutes for foreign minerals are in daily increasing demand.*

- *A few of our SPECIAL KAOLINS supplied in the finest powder form :*

**STOCKALITE**
**DEVOLITE**
**COLWHITE**
**SPESWHITE**
**SUPREME**

- *TALC SUBSTITUTES :*

**TAKOLIN · TAKOLITE, Etc.**

- *BARYTES SUBSTITUTE :*

**KALYTES**

**PRODUCERS :**

**ENGLISH CLAYS LOVERING POCHIN & CO. LTD.**

*HEAD OFFICE, MINES and MILLS at*

**ST. AUSTELL CORNWALL**

*Offices also at London, Stoke, Manchester, Newcastle, Edinburgh, etc.*
*Depots and Stores in many parts of the country.*

Telegrams : Universal, St. Austell. 'Phone : 482 St. Austell.

# NOTICES TO AUTHORS OF PAPERS

1. All Scientific Communications for the Journal should be addressed to "The Secretaries, Chemical Society, Burlington House, W.1." Papers to be read before a meeting of the Society are selected by the Secretaries.

2. A paper is not normally considered for publication in the Journal unless at least one of the authors is a Fellow of the Society, but in exceptional circumstances the Council is prepared to consider papers submitted by non-Fellows.

3. An author must submit with every paper a signed form of declaration that to the best of his knowledge the paper does not contain any information that contravenes the Official Secrets Act.

4. An author engaged in any Government Department or similar body associated with the prosecution of the war must submit with his paper a written declaration from such Department or body that he has received authority to submit the paper for consideration for publication in the Journal.

5. All papers should be submitted in typescript in double-line spacing. Footnotes in papers add considerably to the cost of printing; authors are requested, therefore, not to use them unless necessary.

6. Every paper should be prefaced by a short summary setting forth briefly and in simple language the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. The summary should be such as to enable any chemist to obtain a clear idea of what the investigation has achieved and should normally be from 50—250 words in length.

7. If he desires to do so, an author may send with the paper, for consideration by the Publication Committee, a confidential report by a Chemist of standing to whom the paper has been submitted.

8. The Publication Committee invites authors who publish series of related papers in the Journal to submit, at suitable intervals, papers reviewing their previously published work (suspended during the war).

9. The Society reserves the right to retain the Manuscript and illustrative drawings of all papers sent to it, and authors are therefore advised to keep copies. This right is not usually exercised in respect of illustrative drawings. When papers have been accepted for publication the authors are not at liberty, save by permission of the Council, to publish them elsewhere until such papers have appeared in the Journal of the Society. Papers which are retained by the Council after being judged unsuitable for publication in the Journal are deposited in the Archives of the Society.

10. Communications which have appeared in any other Journal shall not be published in the Journal of the Chemical Society unless this course is approved by a special vote of the Council.

11. The address to which proofs are to be sent should be written on every paper.

12. Authors resident overseas are requested to name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

13. Illustrations accompanying the papers must be carefully drawn, preferably **twice** the size of the finished block (max. width, 4½ inches), **in Indian ink,** on **smooth white Bristol board or paper.** Any illustration which exceeds four times the size of the finished block will be returned to the author for re-drawing to a smaller scale. Lettering on the drawings, whether on the margin or in the body of the drawing, must not be in ink but must be inserted *lightly in blue pencil.* Authors may, if they wish, submit in the first place clearly drawn pencil sketches instead of the completed diagrams, which, however, must be supplied before publication. Further information can be obtained from Dr. C. Smith, Dillions, Handcross, Sussex.

14. If any Author requires more than the number of reprints (without wrappers) allowed by the Society, namely, 10 plus 10 extra for each author in excess of one, or desires to receive his reprints in wrappers and is willing to pay the extra cost thereby involved, he should inform Dr. Smith at the time he sends in the corrected proof. Extra copies will be supplied at rates which can be obtained from the Editor.

B T L

# NON-CORRODIBLE NON-MAGNETIC WEIGHTS

The principle of plating brass weights with gold, platinum, rhodium, or other chemical resistant metal has always the drawback that a thin covering of the metal does not necessarily behave similarly to the massive metal.

The weights illustrated are formed of a special nickel-chromé alloy which possesses remarkably resistant properties to corrosion.

They are of first class accuracy, the maximum limit of error of the individual weights being in many cases better than that specified for Class A—N.P.L.

*Full particulars on request.*

## BAIRD & TATLOCK (LONDON) LTD.

*Makers of Scientific Apparatus*

14-17 ST. CROSS STREET, LONDON, E.C.1

# CHEMICALS IN INDUSTRY

Our arrangements with producers here and abroad still permit us to distribute raw materials of standard quality both for home trade and export for use in the following industries:

**CERAMICS · ELECTRIC BATTERIES · ENAMELS EXPLOSIVES · FOUNDRIES · GALVANIZERS GLASS · INSECTICIDES · INDUSTRIAL EMULSIONS · JOINTLESS FLOORING LEATHER · MANUFACTURING CHEMISTS MINING AND METALLURGY · OILS AND FATS · PAINT · PHOTOGRAPHY · RAYON REFRACTORIES · RUBBER · SOAP · TEXTILES WATER PURIFICATION**

Arsenic and Activated Carbon, Decolorising Carbon, Bentonite, Battery Carbons, Chrome Alum, Chrome Tans, Graphite, Insecticides, Lead Oxides, Magnesium Chloride, Manganese Oxides, Potash (Caustic, Carbonate, Muriate, Sulphate, etc.), Salammoniac, Sulphocyanides, Zinc Chloride, etc.

●

Distributors of Standard Chemicals and Raw Materials for Great Britain and Overseas Markets. C.I.F. to all parts of the world.

## Bush Beach & Gent Ltd

1, LLOYDS AVENUE, LONDON, E.C.3

*Phones: ROYal 7077/8/9* *'Grams: Beafredma, Fen, London* *Codes: All Standard and Private*

**OUR TRADE MARK**
**YOUR GUARANTEE**

PRODORITE LTD.

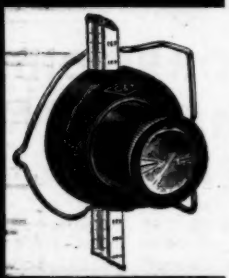
PIONEERS OF
**ACID PROOFING**

FLOORS—TANKS
AND LININGS OF
ALL KINDS BY
SPECIALISTS

•

EAGLE WORKS, WEDNESBURY, STAFFS.
Telephone 0284 (four lines)

***PRECISION***
**MENISCUS READER**



Suitable for use with thermometers and burettes (particularly micro-burettes) where precision readings are required. It is designed to be used with the eye placed 20-30 cm. from the lens, and thus to avoid eye-strain while giving greater comfort during observations. It is provided with back and front sights to eliminate errors due to parallax.

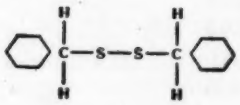
*Details on application*

**GRIFFIN & TATLOCK LTD.**

**LONDON**
Kemble St., W.C.2
**MANCHESTER**
19 Cheetham Hill Rd., 4
**GLASGOW**
45 Renfrew St., C.2
**EDINBURGH**
7 Teviot Place, 1

FINE HPL CHEMICALS

**DIBENZYL DISULPHIDE**



Available as fine white crystals in two grades:

Pure - melting point 70 – 72° C.
Technical- „ „ 65 – 68° C.

SUGGESTED USES:

Plasticiser
Extreme Pressure Lubricant
Rubber Antioxidant

Enquiries invited from
HERTS PHARMACEUTICALS LTD.,
WELWYN GARDEN CITY
Makers of fine organic chemicals

**WRITE FOR SAMPLES and TECHNICAL INFORMATION..**

PURE CRYSTAL **ALUM**
OF UNVARYING COMPOSITION & UNRIVALLED PURITY

**SULPHATE OF ALUMINA**
ALL GRADES SUPPLIED

**"ALUMINOFERRIC"**
THE CHEAPEST FORM OF SULPHATE OF ALUMINA

**ACTIVATED ALUMINA**
ADSORBENT AND CATALYST

**SODIUM ALUMINATE**
HIGHEST QUALITY · FOR WATER SOFTENING

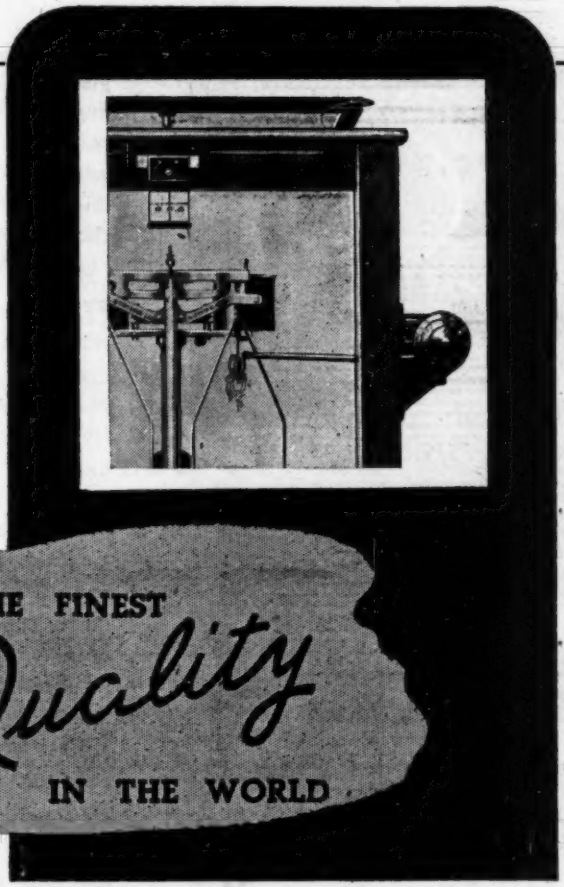
**"NEOSYL"** REGD (AMORPHOUS SILICA)
UNIQUE LIGHTNESS & FINENESS

**"TYPHOX"** AND TITANIUM POTASSIUM OXALATE
IDEAL MORDANTS FOR LEATHER DYEING

**TITANOUS SULPHATE**
A MOST POWERFUL & ECONOMICAL STRIPPING AGENT

**PETER SPENCE & SONS LTD**
NATIONAL BUILDINGS · MANCHESTER 3
LONDON OFFICE: 4 HANGER GREEN · EALING · W.5

G.I




**Rapid, accurate precision weighing made possible with the "Multi-weight" device—**
*Oertling design saves Chemists' time!*

All fractional weights added automatically and read off from scale graduated in fifths of a mg. without opening the balance case. No loose weights below 1 gram. Capacity 100 grams. Ask for specification 62 FM.

Oertling

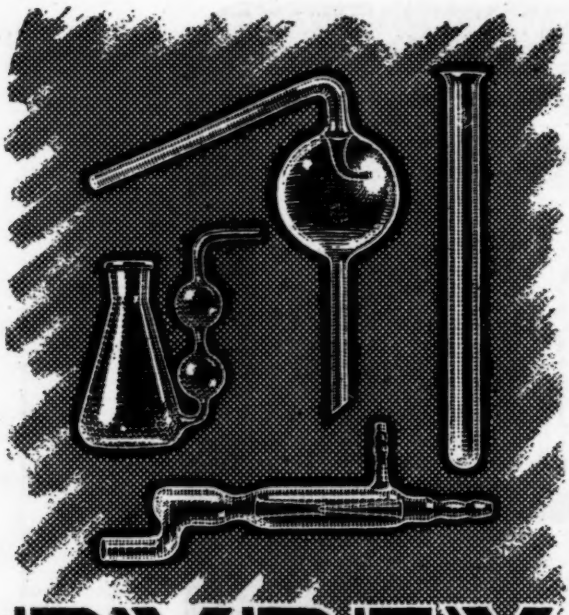
*Note the Address:—*

TELEPHONE
WELbeck 2273

L. OERTLING LTD.
110 GLOUCESTER PLACE,
LONDON . . W.1.
(Near BAKER STREET STATION)

FOUNDED
IN LONDON
BEFORE 1847

TAS/OR.223



**PYREX**

REGD TRADE MARK. BRAND

**SCIENTIFIC GLASSWARE**

**The Key-stone to efficiency in all laboratory work.**

It is essential that all laboratory glassware should possess a degree of stability capable of resisting attacks from acids, while at the same time being immune to the effects of sudden thermal changes.

• • •

PYREX Brand Scientific Glassware fully meets every requirement of daily usage in intricate chemical tests. By reason of its amazingly low co-efficient of expansion (.0000032) it is unaffected by either heat or cold. This characteristic permits us to make the structure of this remarkable Glassware of a more robust build than that of ordinary glass, thus giving it substantial enduring strength, which affords protection against breakage in every-day handling.

• • •

Chemists and scientists will find that PYREX Brand Scientific Glassware maintains, indefinitely, the many vital and reliable properties essential to modern scientific equipment.

*PYREX Brand Scientific Glassware is supplied only through Laboratory Furnishers, but illustrated catalogue and two free copies of our Chemist's Notebook will be sent direct on application to us.*

**Ask for PYREX Brand and see that you get it!**

James A. Jobling & Co. Ltd.

Wear Glass Works,

SUNDERLAND.

T.37.B.

*"Everything for Safety Everywhere"*

**"PROTO," "SALVUS," & "FIREOX"** Self-contained Breathing Apparatus for use in irrespirable atmosphere.

**"NOVITA" & "NOVOX"** (Oxygen and Oxygen + $Co_2$ systems) for persons asphyxiated by poison gas, shock, drowning, etc,

**GAS MASKS** of all types for Naval, Military Civilian and Industrial purposes.

**SIEBE, GORMAN & Co. Ltd., LONDON**

**THE ROYAL INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND**

Founded 1877. Incorporated by Royal Charter, 1885

**APPOINTMENTS REGISTER.**—A Register of Chemists (Fellows, Associates and Senior Registered Students) who are available for appointments, or who are seeking to improve their positions, is kept at the office of the Institute. The facilities afforded by this Register are available (free) to Companies and Firms requiring the services of Chemists, and to Universities, Colleges and Technical Schools requiring Teachers of Chemistry and Technology. A List of Laboratory Assistants is also available.

Particulars of the Regulations and Examinations of the Institute can be obtained (free) on application to the Registrar.

*All communications to be addressed to—*

**The Registrar, The Royal Institute of Chemistry, 30, Russell Square, London, W.C.1**

**UNIVERSITY OF MANCHESTER**

**CHEMISTRY COURSES**

A Prospectus containing full particulars of the LECTURES and LABORATORY COURSES qualifying for the Degrees in Chemistry will be forwarded on application to the REGISTRAR. Applications for admission to the Research Laboratories should be made to the Director of the Chemical Laboratories. The Session commences on Thursday, October 5th.

*The fact that goods made of raw materials in short supply owing to war conditions are advertised in this Journal should not be taken as an indication that they are necessarily available for export.*

MISCELLANEOUS

WANTED back numbers of this journal as follows:—

November and December, 1943.

Indian Jute Mills Association,
Imperial Institute,
London, S.W.7.

# B. BLACK & SON, LTD.

**1 GREEN TERRACE, ROSEBERY AVENUE, LONDON, E.C.1**

*Telephone: TERminus 2030.* *Telegraphic Address: "Gasthermo, Smith, London."*

**THERMOMETER MANUFACTURERS** (Mercury in Glass Type)

*If you use heat—it pays to measure it accurately*

BRITISH MADE THROUGHOUT

Original Makers of the Improved, Gas filled, Permanent Thermometers for Laboratory and Industrial Processes.

Standard Thermometers of the highest accuracy covering over a range from minus 200 to plus 520°C.

The black filling in etchings will resist all solvents with the exception of those that attack the glass itself.

*The mark of precision and efficiency.*

The National Physical Laboratory Certificates supplied with any type.

*Of all the principal Scientific Instrument and Laboratory Apparatus Manufacturers.*

# The Crack Pulverising Mills Ltd.

**GRINDERS TO THE TRADE FOR**

**DRUGS, GUMS, SPICES and CHEMICALS**

**Expert Staff available for Reconditioning of Gums, Drugs, etc., Damaged by Fire or Water.**

*Address all communications to—*

**"THE HAWTHORNS," LEATHERHEAD ROAD, BOOKHAM (SURREY)**

**Works: Tannery Lane, Send, nr. Woking (Surrey).** **Phone: BOOKHAM 2748**

# MANSFIELD OIL-GAS PLANT

## FOR LABORATORIES' GAS SUPPLY

Laboratories without a supply of gas should write for particulars of this Plant which produces gas in a simple manner from any cheap oil such as Solar Oil.... The gas produced has a calorific value of 1,350 B.T.U.'s per cubic foot, and is suitable for use with any appliance designed for use with coal gas and gives perfect oxidising and reducing flames.

**MANSFIELD & SONS**

*Emergency Address:* 4, KINGSMEAD ROAD SOUTH, OXTON, BIRKENHEAD.

*Sole Sales Representatives :—*

# WHATMAN High Grade FILTER PAPERS

*H. REEVE ANGEL & Co., Ltd. 9 Bridewell Pl., London, E.C.4*

**ETHER-TREATED**

**EXTRACTION THIMBLES**

**(SEAMLESS)**

These thimbles have been treated with ether to make them as fat-free as is commercially possible. Very popular for use in Soxhlet apparatus. Supplied in single or double thickness

**FROM ALL LABORATORY FURNISHERS.** **Specify "WHATMAN."**

ium cyanate into carbamide, (2) the interaction of glycerol and oxalic acid, (3) the oxidation of sucrose by nitric acid, (4) preparation of tetranitromethane, (5) the chlorination of ethyl alcohol, leading to a study of alkyl hypochlorites of which the tetra-alkyl compounds are comparatively stable, (6) study of nitro-derivatives of benzil, (7) compounds of the thioparaldehyde type from chloral, (8) quantitative acetylation of phenols in aqueous solution with acetic anhydride, (9) the production of copper mirrors on glass, (10) action of ammonia on esters, where it is shown that, by introducing strongly kationoid centres into the alkyl group, *e.g.*, $CH_3{\cdot}CO{\cdot}O{\cdot}CH<^{CCl_3}_{CH_2{\cdot}NO_2}$, the carbon of the alkyl group becomes so electron-attracting that it and not the carbon of the carbonyl group is attacked by ammonia, yielding acetic acid and $\gamma\gamma\gamma$-trichloro-$\alpha$ nitro-$\beta$-amino-propane, $CCl_3{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NO_2$.

In 1902 he published several papers on the action of halogens on arylazoacetates and related compounds. By diazotising tribromoaniline and coupling the product with ethyl acetoacetate, he obtained ethyl 2 : 4 : 6-tribromophenylazoacetoacetate, $C_6H_2Br_3{\cdot}NH{\cdot}N{:}CAc{\cdot}CO_2Et$. When brominated, this yields products which vary with the conditions. (*a*) In acetic acid solution in presence of water or anhydrous sodium acetate a quantitative yield of the bromo-compound, $C_6H_2Br_3{\cdot}NH{\cdot}N{:}CBr{\cdot}CO_2Et$, is formed by the elimination of an acetyl group; (*b*) in glacial acetic acid or chloroform substitution in the methyl group occurs and the product is $C_6H_2Br_3{\cdot}NH{\cdot}N{:}C(CO_2Et){\cdot}CO{\cdot}CH_2Br$ (I), which is also formed by condensing tribromobenzenediazonium chloride with $\gamma$-bromoacetoacetic ester. Further bromination yields the compound with the group $\cdot CO{\cdot}CHBr_2$ and finally, by elimination of the $\cdot CO_2Et$ group, the poduct $C_6H_2Br_3{\cdot}NH{\cdot}N{:}CBr{\cdot}CO{\cdot}CHBr_2$ is formed. The $\omega$-bromine atom in (I) is reactive and readily replaced by $NH_2$, and the amino-compound so formed reacts with an alcoholic solution of potassium acetate, yielding a 4-hydroxypyrazolone derivative.

A good deal of Chattaway's latest work dealt with the study of the condensation products of chloral, bromal, dichloroacetaldehyde and butylchloral hydrate with phenols, amides, etc. Chloral itself unites with *p*-substituted phenols, the product being of the aldol type $NO_2{\cdot}C_6H_4{\cdot}O{\cdot}CH(OH){\cdot}CCl_3$. This product under the influence of sulphuric acid yields the isomeric phenol, $NO_2{\cdot}C_6H_3(OH){\cdot}CH(OH){\cdot}CCl_3$, which can unite with a second molecule of chloral, forming $NO_2{\cdot}C_6H_3[O{\cdot}CH(OH){\cdot}CCl_3]{\cdot}CH(OH){\cdot}CCl_3$ and by the elimination of water a derivative of 1 : 3-benzdioxan is formed, *viz.*, $NO_2{\cdot}C_6H_3<^{O\text{———}CH{\cdot}CCl_3}_{CH(CCl_3){\cdot}O}$. The presence of a substituent ortho to the OH groups in the phenol inhibits the formation of a dioxan compound. 1 : 3-Dioxan itself can be prepared by condensing *p*-nitrophenol with formaldehyde and removing the nitro-group from the condensation product.

Chloral unites with carbamide, yielding first $CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}CO{\cdot}NH_2$ and finally $CO[NH{\cdot}CH(OH){\cdot}CCl_3]_2$; the second stage, however, does not occur with mono- or unsymmetrical dialkyl- or diaryl-ureas. Other diamides, *e.g.*, oxamide and malonamide, also unite with urea, but with malonanilic acid carbon dioxide is evolved. Chloral condenses with arylhydrazines. With phenylhydrazine the reaction is violent but with halogenated phenylhydrazines simple condensation occurs with the elimination of water and the formation of a hydrazone, which readily loses hydrogen chloride at the ordinary temperature, forming a red azo-compound: $C_6H_2Cl_3{\cdot}NH{\cdot}N{:}CH{\cdot}CCl_3 \longrightarrow C_6H_2Cl_3{\cdot}N{:}N{\cdot}CH{:}CCl_2$.

Chattaway also published several papers on the action of halogens on substituted benzaldehydephenylhydrazones. The halogen substitutes both in the nucleus of the hydrazine residue and also the hydrogen of the original $\cdot CHO$ group ($\omega$-substitution). The $\omega$-halogen is extremely reactive and is readily replaced by $NH_2$ or by $\cdot NH{\cdot}NH_2$. The $\omega$-hydrazino-derivatives react with nitrous acid, yielding derivatives of 1 : 5-diphenyldihydropentazine cyclic compounds with five N-atoms in the ring. $HN<^{CPh{:}N}_{N=N}>NPh$.

Chattaway's influence in the laboratory is best expressed in the words of one of his old students, " Dr. Chattaway was a most stimulating and inspiring influence in the laboratory and filled us with enthusiasm for research. His own tireless energy at the bench and dogged perseverance when things did not go well was an example we shall never forget. Legend has it that the only occasions on which he showed the least signs of losing his temper were when he came across a student working in a slovenly way on a dirty bench. The reprimand invariably had the proper effect. His absorption in his laboratory work was such that, unless reminded, he was apt to forget an engagement or a lecture."

In the usually accepted meaning Chattaway had no hobbies, but apart from his work he had two absorbing passions. The one was for English literature and poetry and the other for the English countryside. His memory was such that after reading a poem twice his knowledge of it was complete. He himself was no mean poet and when a student at Christ Church was awarded the " Constance Naden " gold medal by the Council of the Mason College for a poem entitled " Persephone ". His love of rural England was shown by his annual two or three weeks tour with a friend—in the earlier days on foot, then on cycle and finally by car. He loved the old churches, old monuments and tombs, speculating on the characters of those commemorated. It was always a pleasure to him to engage in conversation with any countryman or woman and to obtain their views on many matters.

Another characteristic was his intense loyalty to institutions and friends. The former is shown by his life-long attachment to the University College, Aberystwyth, and the University of Wales. For very many years he was a member of the Council and of the Court of Governors of the College and also of the University and was a regular attendant at their meetings. He was a past president of the Aberystwyth Old Students'

Association and a past Warden of the Guild of Graduates of the University. His interest in and devotion to educational matters in Wales were such that a well-known Welsh leader once said " I believe Chattaway could have any post in Wales if he wanted it."

For many years he was a member of the Court of Governors of the University of Birmingham and took a keen interest in the work of the University.

To friends of his earlier days he remained intensely loyal. This is shown in his life-long friendships with John Humphrey Davies, afterwards Principal of the Aberystwyth College, and W. H. Lewis, for many years Professor of Chemistry at the University College of the South West at Exeter. Both were fellow students of his at Aberystwyth and at Oxford. I first met Chattaway in 1891 when he was proceeding to Munich and I to Heidelberg. We made a short tour through Belgium and up the Rhine together and he stayed with me in Heidelberg for a few days before going on to Munich; I often met him afterwards in Aberystwyth, Oxford, and latterly in Torquay. Even in his latter days he was a stimulating conversationalist and as stated by one of his friends " In his prime he was brilliant in conversation and was prepared to argue on any topic and on any side, but always in such a whimsical manner that the debate never ran off on unfriendly lines."

In 1894 he married an old Aberystwyth student—Elizabeth Bettany, the second daughter of Thomas Bettany of Birmingham. His only son, who was a King's scholar at Eton and then a Scholar of Christ Church, Oxford, obtained a commission in the Cheshire Regiment in 1915 and was killed in action at Thiepval in 1916. This sad loss was felt by Chattaway for the rest of his life. His widow and only daughter survive him. The daughter, Dr. Margaret Chattaway, took her B.A. degree from St. Hugh's College and subsequently the Ph.D. degree. For some time she was demonstrator in Botany at the Royal Holloway College and then joined the School of Forestry, Oxford, as research botanist. She was awarded the " Elizabeth Sterling " Fellowship at Yale and on leaving there joined the F.A.N.Y.'s and is now a Junior Commander in the Army Education Department.

J. J. SUDBOROUGH.

---

## GERALD TATTERSALL MOODY.

Born March 6th, 1864; died, October 23rd, 1943.

MOODY was born a Londoner and remained one, always residing in the Dulwich area. He chose Chemistry as a career at an early stage when the enlarged facilities for learning it were just coming into being. He was one of the first students of Henry E. Armstrong at Cowper Street, at Finsbury and at the Central Technical College at South Kensington, the Colleges founded by the City and Guilds Institute, and became in due course demonstrator, taking charge of the famous first year " heuristic " course. Later he followed F. S. Kipping as Lecturer. He was a valued member of the brilliant team, Wynne, Kipping, Pope, Lowry, Lapworth, Forster, associated with Armstrong.

Moody will be remembered by many for the part he played in the difficult task of expounding the heuristic method to the first year students, mainly engineers, at the Central Technical College, who did not always take kindly to the doctrine. By practically abolishing the use of textbooks and thereby compelling them to rely almost entirely on their own efforts, particularly in the laboratory work, a method of independence was developed which experience has shown to be of the greatest use in dealing with new problems of every description.

As a very young boy Moody became interested in chemistry through his maternal grandfather, then an old man, who in his earlier days had been associated with Owen in delivering lectures at the Bermondsey Mechanics Institute. In his middle teens, in 1880, he was one of the first students in the temporary laboratory roughly constructed in one of the attics of the Cowper Street School to which H. E. Armstrong and W. E. Ayrton had been apointed teachers pending the building of Finsbury Technical College, which was originally intended as a trade school, but on the advice of Armstrong, Ayrton and Robins was changed to a technical College, with day and evening classes.

Armstong took to young Moody and at once welcomed him into his family circle, encouraging his wider interests, and, finding that they had many tastes in common, took him on geological excursions. Moody was always a keen walker and went off for long walks with his dog in Kent on Saturdays. Later he always took his holidays high up in the mountains in Switzerland. He shared with Armstrong a love and an understanding of gardening and was a regular attendant at the Royal Horticultural Shows. Another interest common to both men was a love of music—he became a frequenter of the Opera.

Moody went on to Finsbury, attending both day and evening classes. When the new building—the Central Technical College at Kensington—was opened, Armstrong was appointed as Professor and Moody went there with him. As the students grew, for it must be noticed that the facilities were provided ahead of the students, novel methods of teaching were developed by each of the four professors—Unwin, Ayrton, Armstrong and Henrici—who became world famous.

His preoccupation with teaching gave Moody little time for research. He published 4 papers in our *Journal* and 11 in the *Proceedings*, one of the most important being on the mechanism of the rusting of iron, always a controversial subject. He gave a paper to the Geological Society on the cause of variegation in coloured rocks.

Moody first took an interest in finance in connection with his mother's capital. He applied his keen analytical mind to the study of investing as a science and finally abandoned teaching to spend his whole time

in the city. He became Chairman or Director of several Investment Trusts and other companies, some of which he led out of difficulties to prosperity. He was very successful and had a high reputation in the City, amassing a considerable fortune which he bequeathed to the Dyers' Company. Armstrong always took pride in Moody's success in Finance as proving the all-round value of the heuristic training.

Moody was exceptionally versatile and capable of great application. In addition to his London external degree of D.Sc., and we believe a degree in Music, he read for the bar and became a bencher of Grays Inn, being called to the Bar in 1910 when he was 46.

He took a considerable part in the affairs of London University, being a member of the Senate and of the Council for external students.

Moody had a long connection with the Worshipful Company of Dyers and was elected Prime Warden in 1936. Moody represented the Dyers' Company on the City and Guilds Institute and served on their various committees as well as on the Delegacy which manages the City and Guilds College. He represented them also on the Medal Committee of the Society of Dyers and Colourists, a connection which led to his election as President of this society in 1936.

He married Hester Sophia Dixon, one of a large family, whose brothers, Walter Dixon, F.R.S., the pharmacologist, and Vice-Admiral Sir Robert Bland Dixon, Chief Engineer to the Navy, both attained distinction.

Moody's early cynicism induced by contact with unruly students developed with advancing age, but he retained and cherished his friendship with many old chemical friends. He and his wife found great pleasure in giving hospitality both in their charming house and gardens on Sydenham Hill and in town.

E. F. ARMSTRONG.

---

## GEORGE SENTER.

### 1874—1942.

THE passing of the late Principal of Birkbeck College will have aroused many thoughts of gratitude and regret in those who love the College. For nearly the whole of the period between the two great wars he directed its development, and its graduates all over the world will remember the inspiration, advice, and practical help he has given them. They will regret that his years of retirement have been all too few and have been darkened by another war.

George Senter was born on January 25th, 1874, at Kildrummy, Aberdeenshire. He was the son of a farmer in a corner of Scotland which escaped most of the troubles of the Stuart times and in which educational opportunities have long been available for all classes. Senter soon showed his quality and won the Bell Scholarship of the Pharmaceutical Society, which brought him to the Society's school in London, where he qualified as a pharmacist. His true love, however, was chemistry and he wooed her in the laboratories of Ramsay, at University College, London, and in those of Ostwald at Leipsig. There he made many lifelong friends amongst the enthusiastic group of students who were founding the new science of physical chemistry. His gifts as teacher, writer and administrator were quickly recognised on his return to London. His most famous book, "Outlines of Physical Chemistry," was first published in 1909 and has run through seventeen editions. This book has inspired generations of students throughout the world and its clarity and common-sense attitude have been greatly valued. In 1912 the title of Reader was conferred on him and in the same year he was elected a member of the Senate of London University. In 1914 he was appointed Head of the Chemistry Department of Birkbeck College. It is an interesting sidelight on the views held thirty years ago that this appointment required him to resign from the Senate. In 1918 he became Principal of the College and thereafter the story of his life is one of outstanding service to the College and the University.

His first task as Principal was to revive the life of the College after the damage caused by the first world war. This was made more difficult by the large influx of students who crowded both day and evening classes. The writer well remembers the problems which arose in 1919 to 1921 with accommodation packed beyond capacity and the staff all too few and often inexperienced. Yet students, staff, and Principal were full of enthusiasm and these hectic years are a happy memory. During this period two important events occurred which were largely due to the efforts of the Principal. The sports ground at Greenford was acquired in 1919 and in 1921 the College was recognised as a School of the University. This recognition was for five years in the first place: it was renewed in 1925 and finally was granted without time limit in 1932. The report of the University inspectors which led to this decision summarised the progress of the College in the following words, "The College has expanded quickly in many directions and fulfils with increasing efficiency its original aim, namely, that of providing culture and instruction in the evening for students who are otherwise occupied in the daytime and who seek the degrees of the University. We believe that in this aim and achievement Birkbeck College is unique in the British Isles."

Two features of the progress of the College in the twenties and early thirties may be mentioned, since they were particularly encouraged and fostered by the Principal. The first was the development of a corporate student life which presented many difficulties in an evening College. Senter took a special interest in the activities of the Students' Union and was regularly to be found at the sports ground at Greenford not only on the high days of special athletic events but also on the pleasant informal occasions of the ordinary week-end activities. The other feature of College life on which Senter laid special stress was the development of postgraduate

work. The success of this is shown by the fact that from 1931 until the outbreak of the present war about 180 postgraduate students registered each session. They were divided almost equally between the Faculties of Arts and Science.

As a physical chemist Senter made a number of important contributions to the science, and though he was Principal of Birkbeck College he for many years remained Head of the chemistry department and directed the work of a group of research students. His earlier work was concerned with the development of biological applications of the new science of physical chemistry and included some work on enzyme reactions. His major work was, however, the application of methods of chemical kinetics in the problem of the Walden inversion. This was pioneering work undertaken at a time when little was known about the complexity of such reactions. In a series of papers published in the *Journal* of the Chemical Society between 1914 and 1925 Senter and his students shed a good deal of light on the problem of replacement reactions in solution. After 1925 his duties as Principal compelled him to give less and less time to this work. More recently Ingold and his collaborators have made important advances in this field and have paid tribute to the valuable work which came from Senter's laboratory. Senter's contributions to the Faraday Society's discussions must also be mentioned; in particular his introductory paper to the discussion on " Passivity " is a model of clearness as well as a summary of valuable information. Of his other publications his " Outlines of Physical Chemistry " has already been mentioned; his " Textbook of Inorganic Chemistry " has also been of great help to students. Both books are characterised by extreme clearness of expression and a common-sense attitude towards theory which are especially helpful to beginners.

It would be tedious to recite all the University appointments which Senter held. Suffice it to say that he served on the Senate from 1912 to 1914, 1922 to 1923 and from 1928 to 1939. The last period he was ex-officio a member of the Senate in virtue of his position as Principal of the College. This brought Birkbeck into line with other large colleges whose heads are automatically Senators. In 1934 to 1935 he was Deputy Vice-chancellor. He served on many committees and boards; of these chemists will remember his helpfulness on the Board of Studies in Chemistry, of which he was Chairman for thirteen years.

S. Sugden.

---

## 94. *The Reduction Potentials of Acridines, with Reference to their Antiseptic Activity.*

By B. Breyer, G. S. Buchanan, and H. Duewell.

The behaviour at the dropping-mercury electrode of acridine and of a number of its derivatives has been studied. It was found that the acridines are reduced in two stages, the first leading to the formation of a monohydroacridine radical, the second to dihydroacridine. Diffusion currents and concentrations of most acridines were found to be mutually proportional in solutions from $10^{-3}$ to $10^{-5}$ M. The reduction potentials were measured through the pH range from 2 to 12, and, as a result, this further physical property has been correlated with the known relationship between degree of dissociation and biological activity of acridines. It was found that those members having a more negative reduction potential than — 0·400 v. (against the normal hydrogen electrode) at pH 7·3 are most active biologically.

In the endeavour to correlate physical and biological properties of acridines, Albert, Goldacre, and Rubbo have investigated the basicities and partition coefficients of a series of aminoacridines (*Nature*, 1941, **147**, 332, 709), and shown that the members most active against bacteria are at the same time the most basic and the most hydrophilic.

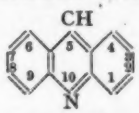
In order to throw further light on the mode of action of acridine drugs, it seemed desirable to measure their reduction potentials and try to correlate the results with the antiseptic activity, especially as McIlwain has recently shown (*Biochem. J.*, 1941, **35**, 1311) that the antiseptic action of aminoacridines can be prevented by adding a hydrogen carrier to the broth in which the bacteria are growing. The effective hydrogen carriers were riboflavin, methylene-blue, and pyocyanine, substances lying within the range $E_h^\circ$ (standard potential at a given pH) from + 11 down to — 275 millivolts at pH 7. This inhibition can itself be " inhibited " by adding more proflavine, and so on. McIlwain concludes that proflavine acts (*inter alia*) by competing with a biological chemical, to wit a hydrogen carrier, within the bacteria for a place in an enzyme system vital to its growth.

It seemed therefore important to know the reduction potential values $E^{\circ\prime}$ of the aminoacridines to find out: (1) whether the active members are as negative in $E^{\circ\prime}$ as would be required if the above theory is true; and (2) whether the ratio of the $E^{\circ\prime}$ values of the active to the biologically inactive aminoacridines is such as to suggest that the value of the redox potential can be used as a measure of their activity, thus eliminating lengthy bacteriological work.

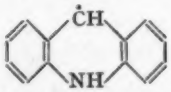
The reduction potentials of the acridine series now reported have been obtained with the help of the dropping-mercury electrode, *i.e.*, by polarography. The application of this electrode for measurements of this kind seems justified, in spite of objections that have sometimes been raised, because it has been shown beyond doubt that the polarographic half-wave potential of organic substances, from an electrochemical point of view, is identical with the $E^{\circ\prime}$ obtained by any other electrode arrangement (cf., *e.g.*, Müller and Baumberger, *Trans. Electrochem. Soc.*, 1937, **71**, 181), provided of course that the electrode reaction be reversible, a limitation which applies equally to the " classical " way of measuring redox potentials. Furthermore, polarography is superior to the

usual method of estimating redox values when the number of electrons involved in the electrochemical reaction (or, for that matter, the number of hydrogen atoms consumed in the reduction of organic molecules) is to be established. The commonly used method relies for this kind of measurement fundamentally on the Nernst equation, which, however, is valid only when the electrochemical process is perfectly reversible. Polarographically the number of electrons (or hydrogen atoms) taken up in the reduction is estimated with the help of Ilkovič's equation (*Coll. Czech. Chem. Comm.*, 1934, **6**, 498), which, being independent of the condition of electrochemical equilibrium, gives most satisfactory results.

At the dropping-mercury electrode, acridine and its derivatives are reduced in two steps of equal height. By applying Ilkovič's equation, *viz.*, $I_d = 605nD^{\frac{1}{2}}Cm^{2/3}t^{1/6}$ [where $I_d$ is the average diffusion current in microamp. (μa.) during the life of a mercury drop, $n$ the number of faradays necessary to reduce one mol. of the substance, $C$ the concentration of the substance in millimols./l., $m$ the rate of flow of mercury from the capillary in mg./sec., $D$ the diffusion coefficient in cm.²/sec., and $t$ the drop time in seconds], it was found that only one hydrogen atom is taken up with each step, meaning that the first product of reduction is a free radical. For this and the other measurements, a very slow-dropping capillary has been used, for it has been found that the results so obtained are more accurate. Some experimental details, by way of example, are given below :




Acridine.




Monohydroacridine radical.

Acridine in borate–HCl buffer, pH 9; temp. 0°.

*First step :* $I_d = 0{\cdot}130$; $D_0 = 4{\cdot}63 \times 10^{-6}$; $m = 0{\cdot}577$; $t = 8{\cdot}87$; $C = 0{\cdot}1$. Therefore $n = 1{\cdot}02$.

*Second step :* $I_d = 0{\cdot}132$; $D_0 = 4{\cdot}63 \times 10^{-6}$; $m = 0{\cdot}660$; $t = 7{\cdot}52$; $C = 0{\cdot}1$. Therefore $n = 0{\cdot}96$.

The diffusion coefficients at infinite dilution ($D_0$) were calculated from Nernst's equation, $D_0 = \boldsymbol{R}T\Lambda_0/nF^2$. The value for $\Lambda_0$ (equivalent conductivity at infinite dilution) was obtained by Albert and Goldacre (J., 1943, 454) on 2-amino-10-methylacridinium bromide at 0°, and found to be 19.

The diffusion current for $10^{-4}$ M solutions of acridines, calculated from Ilkovič's equation, is 0·135 μa. at 0°. The values actually found for the different members of the series vary within a range of ± 5% from the figure theoretically required. The diffusion current varies by 1·12% for 1°. The proportionality between step height and concentration is very good within the range of $10^{-3}$—$10^{-5}$ M, except for acridine and 4-aminoacridine, which show proportionality only within the range $10^{-4}$—$10^{-5}$ M. In these two instances, at concentrations higher than $10^{-4}$ M, the whole shape of the polarographic curve is altered as well. Three steps appear instead of the usual two. In the case of acridine the height of the first step remains unchanged within the whole range from $10^{-3}$ to $10^{-4}$ M. At the same time the $E_{\frac{1}{2}}$ (potential of the dropping mercury electrode at the midpoint of the step, referred to the normal hydrogen electrode) is shifted from − 0·042 v. to − 0·099 v. at pH 2, and from − 0·054 v. to − 0·124 v. at pH 4. The height of the second step diminishes with dilution, but there is no proportionality between dilution and step height. At a concentration of $10^{-4}$ M this second step disappears altogether. The potential shift with increasing dilution is considerable : at pH 2 from − 0·329 v. at $10^{-3}$ M to − 0·473 v. at $1{\cdot}25 \times 10^{-4}$ M, and at pH 4 from − 0·314 v. to − 0·454 v., respectively. The third step consists of a slow, drawn-out rise, and starts approximately at − 0·410 v. (pH 2) and − 390 v. (pH 4). It disappears at a dilution of $2{\cdot}5 \times 10^{-4}$ M. For 4-aminoacridine, the height of the first step diminishes with dilution, but considerably less than is required theoretically. The potential is shifted from − 0·143 v. at $10^{-3}$ M to − 0·166 v. at $10^{-4}$ M at pH 2, and from − 0·174 v. to − 0·200 v. at pH 4. The height of the second step, as in the case of acridine, diminishes slowly with dilution, to disappear at a concentration of $10^{-4}$ M. The potential shifts from − 0·313 v. at $10^{-3}$ M to − 0·348 v. at $1{\cdot}25 \times 10^{-4}$ M at pH 2, and from − 0·485 v. to − 0·536 v. at pH 4. The third step diminishes with dilution fairly closely to proportionality. The potential shifts from − 0·701 v. at $10^{-3}$ M to − 0·635 v. at $10^{-4}$ M (pH 2), and from − 0·761 v. to − 0·729 v. (pH 4).

The most likely interpretation for this peculiar behaviour of acridine and 4-aminoacridine is that at concentrations higher than $10^{-4}$ M, an intermediate compound between the acridine and the free radical, produced during the first reduction step, is formed. These results are in agreement with those obtained by Lingane *et al.* (*J. Amer. Chem. Soc.*, 1943, **65**, 1348) with 5-phenylacridine, but they interpret the double wave to mean "the formation of a slightly soluble dimer of phenyl- and dihydrophenyl-acridines." It seems doubtful whether this interpretation is correct, for no dihydroacridine is formed at as low a potential as that at which the first wave occurs.

It was interesting to find that the limit of concentration at which acridine will exist as a monomeric substance is $10^{-4}$ M. This was deduced from the fact that no increase in height of the first step occurred as the concentration was increased up to $10^{-3}$ M.

The curve analysis of the acridine steps, by plotting log $i/(i_d - i)$ ($i_d$ = diffusion current, $i$ = current at chosen successive points of the step) against applied E.M.F., yields a straight line as far as the first steps are concerned; but the slope of the curve only exceptionally (*e.g.*, in 1-aminoacridine) approaches the theoretically required value of 59 mv. The values found range from 28 to 82 mv. The curve analysis of the second steps only exceptionally shows a straight line (*e.g.*, in 2 : 8-diaminoacridine) and the slope values vary from 53 to 104 mv., an indication of the irreversibility of the process.

It is obvious that the two reduction processes take place on the nitrogen atom and the $C_5$ atom, respectively, but it had to be established if the first step in the reduction concerns the former and the second step the latter atom, or *vice versa*. From theoretical considerations it is to be expected that the reduction takes place first on the nitrogen atom. This is confirmed by experiment: plotting of the half-wave potentials ($E_{\frac{1}{2}}$) of the first steps against pH yields curves the bends of which correspond to the p$K$ values found by Albert and Goldacre (*loc. cit.*) in the same series of acridines. It is interesting to note in this connection that in the case of acridone, which contains an imino-group, only one step is obtained at the dropping mercury electrode. This wave closely resembles the second reduction step of the other acridine derivatives, as can be seen from the $E_{\frac{1}{2}}$–pH curve: the shift of $E_{\frac{1}{2}}$ with increasing pH follows closely the type of the second steps of the acridines, *i.e.*, the curve shows first a steep slope and then flattens out after the p$K$ bend has been reached.

Table I contains the half-wave potentials of the acridine derivatives studied. With few exceptions (usually due to either maxima formation or extreme closeness of the two steps) the values are reproducible to approximately ± 10 mv. The maxima are difficult to suppress (only 0·05% of gelatine and in some cases methyl cellulose proved effective), and no $E_{\frac{1}{2}}$ values obtained with the help of suppressors are reported because it was found that their addition affects the $E_{\frac{1}{2}}$ potentials in a completely erratic way.

TABLE I.

(All potentials are negative.)

| pH: | 2. | | 4. | | 5·5. | | 7·3. | | 9. | | 11·8. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Substance. | 1st step. | 2nd step. | 1st step. | 2nd step. | 1st step. | 2nd step. | 1st step. | 2nd step. | 1st step. | 2nd step. | 1st step. | 2nd step. |
| Acridine | 0·099 | (*a*) | 0·124 | (*a*) | 0·157 | 1·063 | 0·313 | 1·057 | 0·472 | 1·069 | 0·731 | 1·065 |
| 1-Aminoacridine | 0·081 | 0·521 | 0·176 | 0·614 | 0·260 | 0·735 | 0·394 | 0·979 | 0·570 | 1·030 | 0·842 | 1·041 |
| 2- ,, | 0·338 | 0·672 | 0·396 | 0·781 | 0·418 | 0·875 | 0·468 | 1·009 | 0·549 | 1·119 | 0·720 | 1·134 |
| 3- ,, | 0·124 | 0·566 | 0·199 | 0·674 | 0·235 | 0·749 | 0·369 | 0·896 | 0·489 | 1·014 | 0·753 | 1·050 |
| 4- ,, | 0·166 | 0·635 | 0·200 | 0·729 | 0·209 | 0·847 | 0·301 | 0·954 | 0·423 | 1·005 | 0·672 | 1·006 |
| 5- ,, | 0·658 | (*a*) | 0·732 | (*a*) | 0·834 | (*b*) | 0·916 | (*b*) | 0·941 | (*b*) | 1·073 | (*b*) |
| 2 : 8-Diaminoacridine | 0·445 | 0·597 | 0·604 | 0·774 | 0·690 | 0·929 | 0·731 | 1·059 | 0·706 | 1·177 | 0·830 | 1·225 |
| 2 : 8-Diamino-10-methylacridinium bromide | 0·422 | 0·588 | 0·560 | 0·728 | 0·634 | 0·889 | 0·650 | 1·055 | 0·639 | 1·153 | 0·627 | 1·218 |
| 2-Chloro-8-aminoacridine | 0·264 | 0·646 | 0·302 | 0·767 | 0·378 | 0·868 | 0·402 | (*b*) | 0·473 | 1·077 | (*c*) | (*c*) |
| 3-Hydroxyacridine | 0·162 | 0·257 | 0·202 | 0·318 | 0·229 | 1·029 | 0·369 | 1·030 | 0·506 | 1·050 | 0·884 | 1·046 |
| Acridine-3-sulphonic acid | 0·095 | (*a*) | 0·099 | 0·932 | 0·155 | 0·925 | 0·281 | 0·952 | 0·422 | 0·962 | 0·691 | 0·960 |
| Acridone | (*c*) | (*c*) | — | 0·325 | — | 0·847 | — | 1·191 | — | 1·265 | — | 1·391 |

(*a*) Hydrogen step overlaps. (*b*) Maximum formation. (*c*) Insufficiently soluble.

The buffers used were: pH 2 and 4, citrate–hydrochloric acid; pH 5·5 and 7·3, phosphate; pH 9, borate–hydrochloric acid; pH 11·8, borate–sodium hydroxide, all after Sörensen. All solutions were $10^{-4}$ M with regard to the acridine derivative. A saturated calomel electrode served as an anode, but the potentials reported refer to the normal hydrogen electrode, as customary in biological work. The measurements were carried out in a thermostat at 25°.

The reduction potentials for 2-amino-, 5-amino-, and 2 : 8-diamino-acridine are noticeably higher than for the other compounds of the series, a fact exhibiting a parallelism with the p$K$ values of these compounds as found by Albert and Goldacre (*loc. cit.*), who showed convincingly that these variations are due to ionic resonance phenomena. This parallelism is particularly evident at lower pH values, whereas the differences are less pronounced at a pH of 9 and over.

The results of this investigation indicate that there is a definite relationship between reduction potentials and chemotherapeutic activity of the acridines, in the sense that those members which have a more negative $E_{\frac{1}{2}}$ value for the first step than − 0·400 v. at pH 7·3, are biologically the most active (see Table II).

TABLE II.

| Substance. | $E_{\frac{1}{2}}$, v. (pH 7·3). | Averaged bacteriostatic index.* |
|---|---|---|
| 5-Aminoacridine | −0·916 | 4·6 |
| 2 : 8-Diaminoacridine | −0·731 | 4·6 |
| 2-Aminoacridine | −0·468 | 4·2 |
| 1-Aminoacridine | −0·394 | 0·8 |
| 3-Aminoacridine | −0·369 | 1·6 |
| Acridine | −0·313 | 1·2 |
| 4-Aminoacridine | −0·301 | 1·8 |

* Values from Albert and Goldacre (*loc. cit.*): they are expressed in powers of 2.

In the case of the less active members of the series the order of $E_{\frac{1}{2}}$ values does not run parallel with the bacteriostatic index, which is easily understood since the biological activity of acridines must be governed by other factors in addition to the reduction potential. For instance, it has been shown by Albert, Goldacre, and Rubbo (*loc. cit.*) and by Rubbo, Albert, and Maxwell (*Brit. J. Exp. Path.*, 1942, **23**, 69) that the degree of dissociation and the partition coefficient have a direct bearing on the bacteriostatic index of these compounds. There seems to be little doubt, therefore, that the biological activity of the acridines is not connected with a

single physical or chemical property, but is the result of the sum total of such properties. It is evident from this investigation that the active members of the series have reduction potentials so negative that they cannot be reduced under the conditions prevailing in the living organism. The highly negative reduction potential of the biologically most active acridines suggests that they react, by means of their basic groups, with a respiratory enzyme system, the activity of which is inhibited by the combination with the difficultly reducible acridine derivative. Such substances as thionine or methylene-blue, on the other hand, although their chemical structure and basicity are similar to those of the active acridines, display a negligible antiseptic value, most probably because of the fact that their redox potential is very near to that of the living cell. Therefore, their combination with the enzyme will not only not impair but, on the contrary, even effectively take the place of the respiratory system of the cell where this has been damaged by the previous administration of toxic substances (cf. *e.g.*, McIlwain, *loc. cit.*, and Jancso and Jancso, *Z. Immunitäts.*, 1936, **88**, 275).

We are greatly indebted to Dr. A. Albert, not only for the compounds used in this investigation, but also for very helpful discussion during the progress of the work. We also wish to thank Mr. J. B. Willis for preliminary work done in connection with this investigation. One of us (B. B.) is indebted to the University of Sydney for a Commonwealth Research Grant which made the work possible.

UNIVERSITY OF SYDNEY. [*Received, April 19th*, 1944.]

## 95. *The Synthesis of Dimethyl Dimethylene* l-*Idosaccharate.*

By W. G. M. JONES and L. F. WIGGINS.

Methylenation of the calcium salt of *l*-idosaccharic acid has been effected, and the resulting dimethyl dimethylene *l*-idosaccharate shown to be identical with the ester obtained by the epimerisation of dimethyl dimethylene *d*-glucosaccharate and dimethyl dimethylene *d*-mannosaccharate.

THE transformations taking place when dimethylene glucosaccharic acid or its dimethyl ester is treated with boiling baryta solution have been described by Haworth, Jones, Stacey, and Wiggins (this vol., p. 61). The product in either case was an isomeric dimethylene saccharic acid which could likewise be obtained by the treatment of dimethyl dimethylene *d*-mannosaccharate with hot alkali. It was postulated that the reaction taking place was one of epimerisation at $C_5$ in the case of the *d*-glucosaccharate and at $C_2$ and $C_5$ in that of the *d*-mannosaccharate, leading to the formation of the hitherto unknown dimethylene *l*-idosaccharic acid. This deduction has now been completely verified by the synthesis of the dimethyl ester of dimethylene *l*-idosaccharic acid from *l*-iditol.

*l*-Iditol was prepared by the hydrogenation of *l*-sorbose over Raney nickel, and separated from the accompanying *d*-sorbitol by acetylation of the product and subsequent fractional crystallisation of the hexa-acetates. Catalytic deacetylation of the *l*-iditol hexa-acetate gave crystalline *l*-iditol. Oxidation of the alcohol was effected by means of nitric acid, and *l*-idosaccharic acid isolated as the calcium salt. Methylenation of this salt by treatment with paraformaldehyde and concentrated sulphuric acid, followed by esterification with methyl alcohol, gave dimethyl dimethylene *l*-idosaccharate, shown to be identical with the material obtained by epimerisation of dimethyl dimethylene *d*-gluco- and *d*-manno-saccharate.

### EXPERIMENTAL.

l-*Iditol Hexa-acetate.*—*l*-Sorbose (50 g.) in water (300 c.c.) was hydrogenated over Raney nickel at 145° and 90 atm. for 6 hours. The filtered solution was evaporated to a syrup, which was boiled for ½ hour with acetic anhydride (200 c.c.) and fused sodium acetate (25 g.). The product was poured into ice-water and the crystalline precipitate which separated was filtered off, washed with water, dried, and fractionally recrystallised from alcohol; two fractions were thus obtained, *viz.*, hexa-acetyl *l*-iditol (30 g.), m. p. 122°, $[\alpha]_D^{15°}$ −24·8° (in chloroform; *c*, 5·63), and hexa-acetyl *d*-sorbitol (35 g.), m. p. 98°. Bertrand (*Bull. Soc. chim.*, 1905, **33**, 166) gives m. p. 121·5° and $[\alpha]_D$ −25·7° (in chloroform) for hexa-acetyl *l*-iditol.

l-*Iditol.*—Finely powdered *l*-iditol hexa-acetate (14 g.) was suspended in dry methyl alcohol (300 c.c.), sodium (50 mg.) added, and the mixture shaken overnight until solution was complete. Evaporation gave *l*-iditol in quantitative yield as a syrup which slowly crystallised on keeping in a desiccator. It was used as such for the following experiment.

*Oxidation of* l-*Iditol.*—*l*-Iditol (5 g.) was vigorously oxidised by warming with 60 c.c. of nitric acid (*d* 1·15) on the boiling water-bath; excess of nitric acid was removed by repeated evaporation with addition of water from time to time, and the syrup finally obtained was diluted and neutralised at 70° with sodium hydroxide solution. Hydrated calcium chloride (5 g.) was then added, and the precipitated calcium *l*-idosaccharate (6 g.) removed by filtration, washed with water, and dried in air.

*Methylenation of Calcium* l-*Idosaccharate.*—The calcium salt (3 g.) was mixed intimately with paraformaldehyde (2 g.), concentrated sulphuric acid (1·5 c.c.) added, and the mixture stirred to a thick paste and warmed over a bare flame for 30 minutes. Dry methyl alcohol was added, and insoluble calcium sulphate filtered off. The methyl-alcoholic solution was boiled under reflux for 2 hours, and the product crystallised from the hot solution. The crystals were collected and recrystallised from aqueous methyl alcohol. A further quantity of the crystals was recovered from the mother-liquors of the esterification; total yield 0·9 g. (Found: C, 45·8; H, 5·3. Calc. for $C_{10}H_{14}O_8$: C, 45·6; H, 5·5%). The crystals melted at 296° and were dimethyl dimethylene *l*-idosaccharate, the m. p. showing no depression on admixture with a specimen of this material prepared by epimerisation of dimethylene *d*-glucosaccharic acid.

The authors are indebted to Professor W. N. Haworth for his interest and to Imperial Chemical Industries, Ltd. (Dyestuffs Division), for a grant in aid of this work.

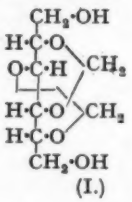
THE A. E. HILLS LABORATORIES,
THE UNIVERSITY, EDGBASTON, BIRMINGHAM. [*Received, April 24th*, 1944.]

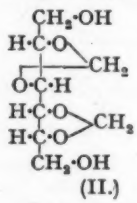
## 96. *The Structure of Monomethylene* d-*Glucosaccharolactone.*

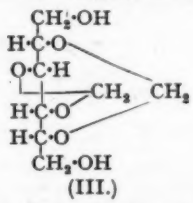
By W. G. M. Jones and L. F. Wiggins.

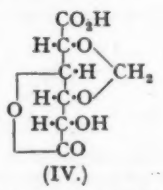
Monomethylene glucosaccharolactone has been oxidatively degraded to monomethylene xylotrihydroxyglutaric acid, shown to be identical with the product of methylenation of xylotrihydroxyglutaric acid. The methylene group is therefore engaged in acetal formation with the hydroxyl groups at $C_2$ and $C_4$ of the carbon chain, and the substance is to be assigned the structure of 2 : 4-monomethylene glucosaccharic acid 3 : 6-lactone. Structures are assigned to the dimethylene derivatives of the saccharic acids and hexahydric alcohols described in previous communications. Methylated derivatives of monomethylene glucosaccharic acid are also described.

In a description of the methylene compounds of saccharic acids and hexahydric alcohols (this vol., pp. 58, 61) we have been confronted with several possibilities for the configuration of the methylene groups in these compounds. For instance, in the dimethylene sorbitol prepared by methylenation of 1 : 6-dibenzoyl sorbitol (Haworth and Wiggins, this vol., p. 58) there are three possible allocations of the methylene groups, involving the hydroxyl groups at $C_2 : C_4$ and $C_3 : C_5$ (I), at $C_2 : C_3$ and $C_4 : C_5$ (II), and at $C_2 : C_5$ and $C_3 : C_4$ (III).


(I.)


(II.)

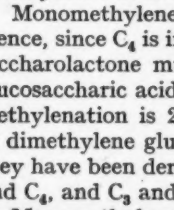

(III.)

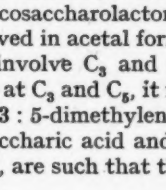

(IV.)

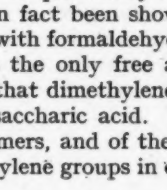
It has been shown that it is possible to oxidise both dimethylene sorbitol and dimethylene mannitol to the corresponding saccharic acids and that, furthermore, these acids epimerise on treatment with hot alkali, giving a common product, dimethylene *l*-idosaccharic acid (Haworth, Jones, Stacey, and Wiggins, this vol., p. 61). Hence, it is to be concluded that all these dimethylene derivatives of the hexahydric alcohols and saccharic acids have the same arrangement of the formaldehyde residues. It has been shown by Haworth and Jones (this vol., p. 65) that monomethylene glucosaccharolactone reacts with methyl-alcoholic hydrogen chloride to give dimethyl monomethylene glucosaccharate, which can be completely methylenated to give dimethyl dimethylene glucosaccharate. If the disposition of the methylene groups in monomethylene glucosaccharolactone can be ascertained, and if it is assumed that no change in position of the methylene group occurs on further treatment with formaldehyde, then the orientation of the methylene groups in all the dimethylene hexahydric alcohols and saccharic acids mentioned previously will have been determined.

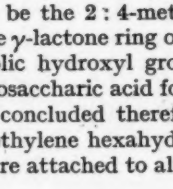
Monomethylene glucosaccharolactone has in fact been shown to be the 2 : 4-methylene compound (IV). Hence, since $C_4$ is involved in acetal formation with formaldehyde, the $\gamma$-lactone ring of monomethylene glucosaccharolactone must involve $C_3$ and $C_6$. As the only free alcoholic hydroxyl groups in monomethylene glucosaccharic acid are at $C_3$ and $C_5$, it follows that dimethylene glucosaccharic acid formed from it by further methylenation is 2 : 4-3 : 5-dimethylene glucosaccharic acid. It is concluded therefore that the structures of dimethylene glucosaccharic acid and its epimers, and of the dimethylene hexahydric alcohols from which they have been derived, are such that the methylene groups in each are attached to alternate carbon atoms $C_2$ and $C_4$, and $C_3$ and $C_5$.

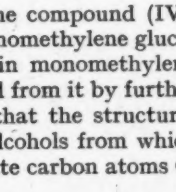
Monomethylene glucosaccharolactone may have one of the structures shown in (IV)—(IX). In these the methylene group joins $C_2$ and $C_4$ (IV), $C_3$ and $C_5$ (V), $C_2$ and $C_3$ (VI), $C_4$ and $C_5$ (VII), $C_3$ and $C_4$ (VIII), $C_2$ and $C_5$ (IX). Formula (VIII) is eliminated because monomethylene glucosaccharolactone is a $\gamma$- and not a $\delta$-lactone,


(V.)


(VI.)


(VII).

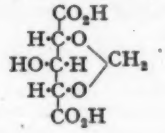

(VIII.)

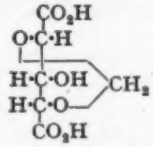

(IX.)

and (IX) is improbable because lactone ring formation would be expected to be sterically hindered by the methylene grouping. The rate of oxidation with lead tetra-acetate of the dimethyl monomethylene glucosaccharate derived from the lactone (Haworth and Jones, *loc. cit.*), determined by Hockett and McClenahan's method (*J. Amer. Chem. Soc.*, 1939, **61**, 1667), was extremely slow, a fact which eliminates structures containing glycollic acid groups, *viz.*, (VI) and (VII). A decision between the remaining possibilities (IV) and (V) was made on the basis of an examination of the products of oxidative degradation of monomethylene glucosaccharolactone.

The oxidative degradation was carried out by means of chromic anhydride in glacial acetic acid solution and a substance corresponding in composition to a dimethyl monomethylene trihydroxyglutarate was isolated. The product was optically inactive and was therefore more probably the *dimethyl* ester of monomethylene

xylotrihydroxyglutaric acid. On hydrolysis, the free acid, m. p. 254°, was obtained. Authentic monomethylene xylotrihydroxyglutaric acid (X), prepared by the procedure described below, had the same m. p. and a mixture

(X.) 

 (XI.)

of the two showed no depression of m. p. This xylotrihydroxyglutaric acid could only have arisen from (IV) : (V) would yield an acid with the arabinose configuration (XI). A Weerman test on the diamide derived from (X) showed the absence of α-hydroxy-groups, thus confirming the allocation of the methylene linkages to $C_2$ and $C_4$. Monomethylene glucosaccharolactone, therefore, has the structure represented by (IV). In the preparation of the reference compound, calcium xylotrihydroxyglutarate, prepared from *d*-xylose by Fischer's method (*Ber.*, 1891, **24**, 1836), was methylenated with paraformaldehyde and concentrated sulphuric acid, and the product isolated as its dimethyl ester. This was identical with the product obtained from the oxidation of monomethylene glucosaccharolactone. Hydrolysis gave the monomethylene xylotrihydroxyglutaric acid. This acid had m. p. 254°, whereas Lobry de Bruyn (*Rec. Trav. chim.*, 1900, **19**, 180) gives m. p. 242°.

By the methylation of dimethyl monomethylene glucosaccharate with silver oxide and methyl iodide, two crystalline products were obtained, *viz.*, *dimethyl* 3 : 5-*dimethyl* 2 : 4-*monomethylene glucosaccharate* and 5-*methyl* 2 : 4-*monomethylene glucosaccharolactone methyl* ester. Oxidation of the former afforded crystalline products which are still under investigation.

In the course of this work the following new crystalline compounds were also prepared : *dimethyl* 3-*methyl* 2 : 4-*monomethylene xylotrihydroxyglutarate* and the *diamide* of the acid.

## Experimental.

*Oxidation of Dimethyl Monomethylene Glucosaccharate with Lead Tetra-acetate.*—The ester (0·0005 mol.) was dissolved in glacial acetic acid (49 c.c.), lead tetra-acetate solution (50 c.c.) [prepared by dissolving lead tetra-acetate (15 g.) in glacial acetic acid (500 c.c.)] added, and the solution made up to 100 c.c. 10-C.c. portions were withdrawn from time to time, run into potassium iodide–sodium acetate buffer, and the liberated iodine titrated with 0·02N-sodium thiosulphate. Hence, the number of g.-atoms of oxygen used per mol. of ester could be calculated : 3 mins., nil; 40 mins., 0·02; 119 mins., 0·02; 257 mins., 0·04. There is, therefore, no rapid oxidation of dimethyl monomethylene glucosaccharate with this reagent.

*Oxidation of Monomethylene Saccharolactone with Chromic Anhydride.*—The lactone monohydrate (2 g.) was suspended in glacial acetic acid (75 c.c.) (the prismatic changed into feathery crystals, corresponding to conversion into the anhydrous form), the suspension stirred vigorously at room temperature, and a solution of chromic anhydride (1·5 g.) in glacial acetic acid (50 c.c.) added dropwise during 2 hours, stirring being continued overnight; the clear green solution was then evaporated under diminished pressure, and water evaporated over the residue in order to remove all the acetic acid. The residue was then dissolved in water, and a slight excess of barium hydroxide solution added to precipitate chromium hydroxide, which was centrifuged off and washed well with cold water. Barium was removed from the combined filtrate and washings by addition of the correct amount of N-sulphuric acid, and after the barium sulphate had been centrifuged off, the filtrate was evaporated to dryness. The residue was esterified by boiling for 6 hours with 2% methyl-alcoholic hydrogen chloride. The acid was then neutralised with silver carbonate, the silver residues filtered off and washed with methyl alcohol, and the filtrate and washings evaporated to dryness. This residue deposited crystals (0·06 g.) after dissolving in a little warm alcohol. The crystals were moderately soluble in water but could be crystallised from a concentrated solution. The substance showed m. p. 203—204° and was optically inactive. A repeat preparation from 5 g. of monomethylene saccharolactone monohydrate gave 0·4 g. of the crystalline product, m. p. 204°, which was *dimethyl monomethylene xylotrihydroxyglutarate* (Found : C, 44·3; H, 5·5; OMe, 27·1; *M*, by titration, 216. $C_8H_{12}O_7$ requires C, 43·7; H, 5·5; OMe, 28·2%; *M*, 220).

2 : 4-*Monomethylene* i-*Xylotrihydroxyglutaric Acid.*—Dimethyl monomethylene *i*-xylotrihydroxyglutarate (27 mg.) was suspended in water and heated with 0·064N-baryta solution (4 c.c.) at 60° for 1½ hours. The correct amount of N/100-sulphuric acid was added, and the solution filtered and evaporated to dryness. Recrystallisation from aqueous alcohol gave monomethylene *i*-xylotrihydroxyglutaric acid as prismatic crystals, m. p. 253—254° (Found : C, 37·8; H, 3·8. Calc. for $C_6H_8O_7$ : C, 37·5; H, 4·1%).

2 : 4-*Monomethylene* i-*Xylotrihydroxyglutarodiamide.*—The dimethyl ester (33 mg.) was suspended in dry methyl alcohol (5 c.c.), and the solution saturated with ammonia at 0°. The ester rapidly dissolved and crystals separated. After being kept for 72 hours, these were filtered off and recrystallised from methyl alcohol; yield, 27 mg., m. p. 286° (Found : C, 37·7; H, 5·0. $C_6H_{10}O_5N_2$ requires C, 38·0; H, 5·3%). A Weerman test for an α-hydroxy-group gave a negative result.

*Dimethyl* 3-*Methyl* 2 : 4-*Monomethylene Xylotrihydroxyglutarate.*—Dimethyl 2 : 4-monomethylene xylotrihydroxyglutarate (33 mg.) was methylated by three treatments with silver oxide and methyl iodide. The product was extracted after each treatment several times with boiling chloroform. A crystalline residue was finally obtained which was recrystallised from ethyl alcohol; yield, 20 mg., m. p. 157° (Found : C, 46·3; H, 6·1. $C_9H_{14}O_7$ requires C, 46·1; H, 6·0%).

*Dimethyl* 3-*Methyl* 2 : 4-*Monomethylene Xylotrihydroxyglutarodiamide.*—The above *ester* (12 mg.) was dissolved in dry methyl alcohol, and the solution saturated with ammonia gas at 0°, whereupon the solution was set aside at 0° for 74 hours. Evaporation at room temperature in a vacuum gave a crystalline *diamide*, which recrystallised from methyl alcohol in the form of prisms (8 mg.), m. p. 295° (decomp.) (Found : C, 41·9; H, 5·8. $C_7H_{12}O_5N_2$ requires C, 41·7; H, 5·9%).

*Dimethyl Monomethylene Xylotrihydroxyglutarate from* d-*Xylose.*—*d*-Xylose (10 g.) was heated with nitric acid (30 c.c.; *d* 1·2) at 40° for 8 hours with occasional stirring (see Fischer, *loc. cit.*). The liquid was then evaporated in an open dish with the addition of water from time to time until most of the nitric acid had evaporated. The solution was then neutralised at the boil with calcium carbonate, filtered, and evaporated to 70 c.c.; the calcium salts then separated; yield, 9 g. A portion (1 g.) of the calcium salt of xylotrihydroxyglutaric acid was mixed with paraformaldehyde (1 g.)

and concentrated sulphuric acid (0·8 c.c.), and the mixture gently warmed for 20 mins.; it was then diluted with dry methyl alcohol (80 c.c.) and refluxed for 4 hours. After neutralisation with barium carbonate, filtration, and evaporation, a semi-solid residue was obtained which yielded crystals of dimethyl monomethylene xylotrihydroxyglutarate, m. p. 203—204°, not depressed in admixture with the product obtained by oxidation of monomethylene glucosaccharolactone. The lactone again showed no optical activity.

*Methylation of Dimethyl Monomethylene Glucosaccharate.*—The ester (10 g.) was dissolved in acetone–methyl iodide (70 c.c.; 1 : 1), and silver oxide (20 g.) added during 10 hours at 50°. Some crystals were formed, and the product was isolated by extraction with acetone. This operation was repeated five times without any attempt at fractionation of the product. The syrupy product finally obtained by distillation of the acetone extract was dissolved in a small amount of acetone and diluted with ether. Crystallisation occurred immediately, and the crystals were filtered off, washed with acetone and ether, and recrystallised from water. *Methyl 5-monomethyl 2 : 4-monomethylene glucosaccharo-3 : 6-lactone* was obtained as long needles (1·2 g.), m. p. 149° (Found : C, 45·9; H, 5·5. $C_9H_{12}O_7$ requires C, 46·0; H, 5·2%).

The mother-liquors were concentrated, the syrupy residue dissolved in the minimum of ether, and the solution set aside. Crystallisation occurred, and the crystals which separated were collected and recrystallised from acetone–ether, forming long needles (3·0 g.), m. p. 96—97° (Found : C, 48·2; H, 6·5; $OCH_3$, 44·7. $C_{11}H_{18}O_8$ requires C, 47·5; H, 6·5; $OCH_3$, 44·6%); these were *dimethyl* 3 : 5-*dimethyl* 2 : 4-*monomethylene glucosaccharate.* The mother-liquors on concentration gave a yellow, fairly viscid syrup which has not been further examined.

*Oxidation of Dimethyl* 3 : 5-*Dimethyl* 2 : 4-*Monomethylene Glucosaccharate.*—The ester (1·0 g.) was dissolved in nitric acid (10 c.c.; *d* 1·42), and the solution gradually heated to 90° by warming in a water-bath, being kept at that temperature for 1 hour; thereafter nitric acid was removed in the usual way. The syrupy residue was boiled with 2% methyl-alcoholic hydrogen chloride (50 c.c.) for 7 hours, the solution neutralised with silver carbonate, and the ester product isolated. It distilled at 165°/0·06 mm. (bath temp.), $n_D^{16.5°}$ 1·4642, yield 0·34 g. The amide was prepared by dissolving a portion of the ester in dry methyl alcohol (2 c.c.) and saturating the solution with ammonia at 0°; m. p. 176° after recrystallising from methyl alcohol (Found : C, 41·3; H, 6·7%).

*Methylation of Esterified Oxidation Product.*—This was methylated by three treatments with methyl iodide (3 c.c.) and silver oxide (1 g.), the product being extracted with chloroform. A fairly viscid syrup was obtained, distilling at 130°/0·02 mm. (bath temp.), $n_D^{20°}$ 1·4457, $[\alpha]_D^{20°}$ + 8·08°.

The amide was prepared by means of methyl-alcoholic ammonia in the usual manner, and appeared to be a mixture of two products : (*a*) recrystallised from water, m. p. 261° (Found : C, 41·8; H, 7·5%), and (*b*) recrystallised from methyl alcohol, m. p. 205° (Found : C, 42·6; H, 7·2%). Neither of these amides, however, has been identified.

The authors are indebted to Professor W. N. Haworth, F.R.S., for his interest, and to Imperial Chemical Industries Ltd. (Dyestuffs Division) for a grant in aid of this work.

THE A. E. HILL LABORATORIES,
THE UNIVERSITY, EDGBASTON, BIRMINGHAM. [*Received, April 24th,* 1944.]

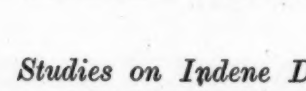
---

## 97. *Studies on Indene Derivatives. Part III. The Constitution and Some Reactions of Bishydroxyindone. The Photochemical Reduction of Triketohydrindene.*

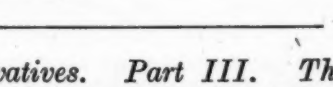
By ALEXANDER SCHÖNBERG and RADWAN MOUBASHER.

The structures of bis-1 : 3-indanedione (I) and 9 : 10-dihydroxynaphthacene-11 : 12-quinone (VII) are discussed. The photochemical reduction of triketohydrindene (XI) by *iso*propyl alcohol yields hydrindantin (XII).

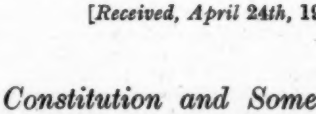
(A) A DARK violet compound usually known as bis-1 : 3-indanedione (bisdiketohydrindene) (I) has frequently been described (Gabriel and Leupold, *Ber.*, 1898, **31**, 1160; Vöswinkel, *Ber.*, 1909, **42**, 467; Dan Radulescu, *Centr.*, 1923, III, 140; Wanag, *Ber.*, 1937, **70**, 274; 1939, **72**, 973), but Hantzsch and Lister (*Annalen*, 1912, **392**, 319) expressed doubt about its ketonic nature and Eok and Marvel (*J. Amer. Chem. Soc.*, 1935, **57**, 1898) have stated that, since only two phenyl groups can be introduced into the molecule by the action of phenylmagnesium bromide, it must exist largely in the dienolic form. We now show that bis-1 : 3-indanedione is the corresponding dienol (IV, R = H) in the solid state, and, as all its reactions in neutral solvents may be explained on the basis of this formula, we propose to replace that name by bishydroxyindone.



(I; R = H.) (II; R = Me.) (IIa; R = OH.)

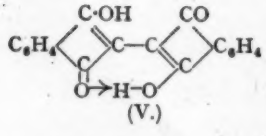


(III.)



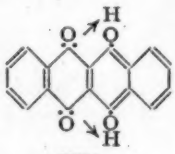
(IV.)

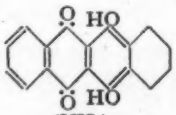
Dimethylbisindanedione (II) is colourless. Its constitution is established beyond doubt by its preparation from 2-methylindanedione (Gabriel and Leupold, *loc. cit.*, p. 1163). According to modern views a compound of constitution (I) should be colourless if (II) is colourless. On the other hand, (IV, R = H) would explain not only the violet colour of the compound but also the facts that it dissolves readily in cold aqueous sodium hydroxide with formation of a brown solution and reacts with diazomethane, giving an orange *dimethyl* ether (III or IV, R = Me). This is easily converted into (IV, R = H) by the action of sulphuric acid. Bishydroxyindone sublimes without decomposition in a vacuum at 340° : it is stable to oxygen at room temperature, but is readily oxidised by oxygen to phthalic anhydride at about 340° in the presence of selenium. We failed to obtain the two forms (III and IV, R = H) of bishydroxyindone possible according to classical theory. It seems probable that (III and IV, R = H) and also (V) represent extreme forms of the same resonance state.

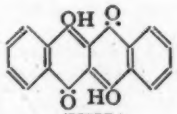


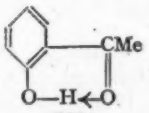
(V.)

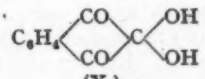
(B) *Comparison of the Reactions of Bishydroxyindone and* 9 : 10-*Dihydroxynaphthacene*-11 : 12-*quinone.*—There is a close relationship between bishydroxyindone (IV, R = H) and 9 : 10-dihydroxynaphthacene-11 : 12-quinone (VII), not only because the former can be very simply converted into the latter by the action of ammonia (Wanag, *Ber.*, 1937, **70**, 274), but also because the corresponding resonance structures of the two substances show close similarities with one another (comp. III, R = H, with VII; IV, R = H, with VIII; V with VI). We have therefore compared the chemical reactivities of the two substances: bishydroxyindone proved to be much the more reactive, possibly owing to the presence of a seven-membered chelate ring (comparatively unstable) (V), whereas in 9 : 10-dihydroxynaphthacene-11 : 12-quinone, which does not react with diazomethane, there is a six-membered chelate ring (comparatively stable) (VI) [comp. also *o*-hydroxyacetophenone (IX), which does not react with diazomethane (private communication by A. Schönberg and Mrs. Abdel Fattah Ismail)]. The same explanation may be given to account for the slight solubility in aqueous alkali at 25° of (VII), in contrast to bishydroxyindone.


(VI.)

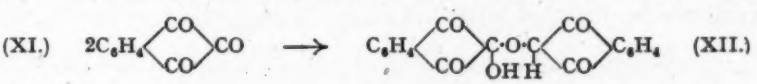

(VII.)


(VIII.)


(IX.)


(X.)

(C) The photochemical reduction of benzophenones by *iso*propyl alcohol in sunlight yields pinacols (Cohen, *Rec. Trav. chim.*, 1920, **39**, 243; Bachmann, *Org. Synth.*, **14**, 8; Schönberg and Mostafa, this vol., p. 67). Very little is known about the photochemical reduction of polyketones under the above conditions. We have found that the red triketohydrindene (XI) (Schönberg and Moubasher, J., 1943, 71) is converted into the colourless hydrindantin (XII), previously prepared in the dark by the action of hydrogen sulphide on

(XI.)  (XII.)

ninhydrin (X) (Ruhemann, J., 1911, **99**, 797). Thus, in this case, the photo-reduction product is not a pinacol, but an ether. The pinacol (II*a*), prepared by Gabriel and Leupold (*loc. cit.*, p. 1164) in the dark, is very different in properties from the photo-product obtained from triketohydrindene.

## Experimental.

*Action of Diazomethane on Bishydroxyindone* (IV, R = H).—The powdered substance reacted vigorously with an ethereal solution of diazomethane, dissolving in the cold after 24 hours; the ether was then driven off, and the residue crystallised from methyl alcohol. The first crystals did not appear uniform under the microscope; after seven recrystallisations, the first crop being used each time, uniform orange crystals of the *dimethyl* ether, m. p. about 112° (decomp.) (depending on the rate of heating), were obtained, easily soluble in methyl alcohol and ether and insoluble in sodium hydroxide solution (Found: C, 75·2; H, 4·8. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%).

The ether was treated with cold concentrated sulphuric acid and then left for several minutes in a water-bath at 50°. The violet solution obtained, when cold, was poured on ice, giving a violet deposit, which, dried and crystallised from nitrobenzene, gave bishydroxyindone, m. p. 297°, undepressed by an authentic specimen.

*Action of Oxygen on Bishydroxyindone in Presence of Selenium.*—Bishydroxyindone (0·5 g.) was powdered with red selenium (1 g.) and heated at 340° (bath temperature) in a current of air. A sublimate of colourless crystals of phthalic anhydride, m. p. 130°, was obtained. The same reaction, carried out with the dimethyl ether (III or IV, R = Me), also gave phthalic anhydride.

*Diazomethane and* 9 : 10-*Dihydroxynaphthacene*-11 : 12-*quinone.*—The quinone, after prolonged treatment with diazomethane as described above, was recovered unchanged. It crystallised easily from dioxan.

*Diazomethane and o-Hydroxyacetophenone* (A. Schönberg and Mrs. A. F. Ismail).—*o*-Hydroxyacetophenone, after treatment with diazomethane during 3 days in the cold, was recovered unchanged and identified by its acetyl derivative and by the violet colour reaction with ferric chloride solution.

*Photochemical Reaction between Triketohydrindene and* iso*Propyl Alcohol.*—Freshly prepared triketohydrindene (XI) (2 g.), suspended in freshly distilled *iso*propyl alcohol (10 g., dried with calcium carbide) in a closed tube, was exposed to sunlight for 10 days. The red substance gradually disappeared and a colourless solid was formed. The excess of *iso*propyl alcohol was then removed in a vacuum, and the residue crystallised from acetone. The photo-product showed the properties of hydrindantin (XII); it turned red at about 200° and decomposed at higher temperatures with evolution of gas, and formed a blue solution with sodium hydroxide (formation of a sodium salt after enolisation). It was crystallised from acetone and air-dried (under these conditions it forms a dihydrate; comp. Ruhemann, *loc. cit.*) (Found: C, 60·0; H, 4·2. Calc. for $C_{18}H_{10}O_6.2H_2O$: C, 60·3; H, 3·9%).

Fouad I University, Cairo, Egypt.

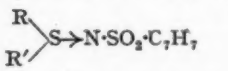
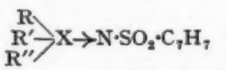
[*Received, February 3rd*, 1944.]

## 98. *Azoxysulphones, their Preparation and Properties, with Observations on the Structure of Diazotates.*

By W. V. Farrar and J. Masson Gulland.

Chloramine-T and related compounds have been shown to condense with a number of aromatic nitroso-compounds to give products which it is proposed to call azoxysulphones. The preparation and properties of some typical members of this new series are described, and the implications of their hydrolysis to diazo-compounds are discussed.

Chloramine-T (sodio-*p*-toluenesulphonchloroamide) reacts readily with thio-ethers, eliminating sodium chloride to give crystalline compounds known as " sulphilimines " (I) (Mann and Pope, J., 1922, 1052); these are clearly similar in structure to sulphoxides, and, when R and R′ are different, can be resolved into optical

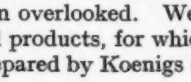
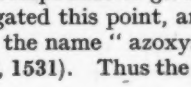
(I.)  (II.) 

isomers (Clarke, Kenyon, and Phillips, J., 1927, 188; Holloway, Kenyon, and Phillips, J., 1928, 3000). Reaction of chloramine-T with thiols and with disulphides gives more complex compounds of sulphilimine type (Phillips and Kenyon, J., 1930, 1225; Alexander and McCombie, J., 1932, 2087).

Analogously, the condensation of chloramine-T with tertiary phosphines (Mann and Chaplin, J., 1937, 527) and arsines (Mann and Pope, *loc. cit.*; Mann, J., 1932, 958) leads to " phosphinimines " (II, X = P) and " arsinimines " (II, X = As), related to phosphine oxides and arsenoxides in the same way as sulphilimines to sulphoxides.

From the above examples, it would seem that, given a compound A capable of being oxidised to A→O, the reaction of A with chloramine-T might lead to A→N·$SO_2$·$C_7H_7$, the group $C_7H_7$·$SO_2$·N functioning as a kind of " pseudo-oxygen." This was shown to be incorrect, however, by Mann and Pope (*loc. cit.*), who found that no reaction occurs between dimethylaniline and chloramine-T to give a compound analogous to an amine oxide (II, X = N).

The possibility that chloramine-T would react with nitroso-compounds to give substances of the type (III) appears, however, to have been overlooked. We have investigated this point, and find that reaction does in fact occur, giving the expected products, for which we propose the name " azoxysulphones " by analogy with the " diazosulphones " first prepared by Koenigs (*Ber.*, 1877, **10**, 1531). Thus the product from nitrosobenzene

(III.)   (III*a*.)

and chloramine-T (III; Ar = Ph, Ar′ = *p*-$C_6H_4$Me) is to be called " *phenyl* p-*tolyl azoxysulphone*," the radical attached to nitrogen being named first. It should be noted that two formulæ (III and III*a*) can be written, differing only in electron distribution; the azoxysulphones, therefore, must be regarded as resonance hybrids between these two unperturbed states, and it seems not improbable that the relative stability of these compounds may be due to this feature, whereas compounds of type (II, X = N), lacking resonance, are too labile to exist.

The reaction between nitroso-compounds and chloramine-T proceeds smoothly in pyridine solution at room temperature or on the water-bath. Exclusion of water is not necessary; in fact a 30—40% yield of azoxysulphone is obtained (though mixed with much troublesome tar) when chloramine-T and *p*-nitrosodimethylaniline are simply shaken overnight in aqueous suspension.

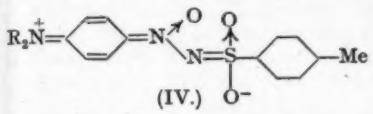
Successful condensations were carried out with chloramine-T and the following nitroso-compounds: *p*-nitrosodimethyl- and -diethyl-anilines, nitrosobenzene, *o*- and *p*-nitrosotoluenes, *m*-nitronitrosobenzene, and *p*-nitrosophenetole. *m*-Dinitrosobenzene (Alway and Gortner, *Ber.*, 1905, **38**, 1899) reacted with two molecules of chloramine-T to give a *bisazoxysulphone*. In addition, sodiobenzenesulphonchloroamide (chloramine-B) was condensed with *p*-nitrosodimethylaniline, and reaction of chloramine-B with nitrosobenzene gave the parent compound of the series, *diphenyl azoxysulphone* (III; Ar = Ar′ = Ph).

Some interesting failures of this synthesis were encountered. *p*-Nitrosophenol reacted violently with chloramine-T in pyridine solution, giving brown tarry materials. 5-Nitroso-2-cresol behaved in the same way; in dilute alcoholic solution the reaction was not so vigorous, but the products were similar. *p*-Nitrosoaniline (Fischer and Hepp, *Ber.*, 1887, **20**, 2471) and *p*-nitrosomethylaniline appeared to react normally with chloramine-T in pyridine, but the products were deeply-coloured, amorphous materials only slightly soluble in organic solvents, giving faintly red solutions; they could not be satisfactorily purified, and as they had no basic properties it seems likely that their constitution is more complex than that of the simple azoxysulphone (III, Ar = *p*-$NH_2$·$C_6H_4$ or *p*-NHMe·$C_6H_4$; Ar′ = *p*-$C_6H_4$Me). This anomalous behaviour is probably to be connected with the fact that all four of these nitroso-compounds can become quinonoid derivatives by prototropic change. In this connection it is noteworthy that *p*-benzoquinone itself reacts readily with chloramine-T when their solutions in cold alcohol are mixed, giving ill-defined, brownish-purple substances which we have not investigated.

No combination appears to occur between chloramine-T and either *N*-nitroso-compounds, typified by phenyl-

methylnitrosoamine, or azobenzene under the conditions which suffice for *C*-nitroso-compounds. Our experiments on these points have, however, not been exhaustive.

The azoxysulphones so far prepared by us fall into two well-defined groups. Those not containing a dialkylamino-substituent (such as diphenyl azoxysulphone) are very pale yellow, well-crystallised substances, insoluble in water, but fairly readily soluble in organic solvents; they melt (with one exception) in the region 106—128° without decomposition. The only bisazoxysulphone yet prepared is also pale yellow, though less soluble, and melts at 208° with decomposition. The *p*-dialkylamino-derivatives, on the other hand, are very deeply coloured (red, red-brown, or bronze) and sparingly soluble in low-boiling organic solvents; they all melt around 180° with decomposition. These properties indicate a certain polarity in their structure, which may be perhaps represented by resonance of the azoxysulphone form with a quinonoid form such as (IV). This view is supported by the fact that in concentrated acid solution, where hydrolysis is absent, the cation of the salt is colourless, having presumably the structure (III and III*a*, Ar = $\overset{+}{N}HR_2Ph$–).



(IV.)

Compared with the closely-related diazosulphones, the azoxysulphones are stable compounds. Their reactions have mainly been studied by using the readily accessible phenyl *p*-tolyl azoxysulphone.

Reduction of the azoxysulphone with zinc dust and acetic acid in alcoholic solution gives a good yield of the phenylhydrazide of toluene-*p*-sulphonic acid. This is valuable confirmatory evidence of the structure assigned to the compound. The azoxysulphone is attacked only slowly by boiling acid, neutral, or alkaline permanganate, acetone–permanganate solution, or acid potassium dichromate. Cold concentrated nitric acid has no action, and small quantities of the azoxysulphone can be crystallised unchanged from the warm acid. Bromine in chloroform is not decolorised. This resistance to substitution could be predicted on constitutional grounds.

When heated alone, all the monoazoxysulphones decompose with some violence at about 180—200°; sulphur dioxide is evolved and a tarry or coke-like residue is left.

Phenyl *p*-tolyl azoxysulphone is not significantly affected by prolonged boiling with dilute (2N) acids and alkalis. Distillation with 50% sulphuric acid, however, affords considerable quantities of phenol (identified as 2 : 4 : 6-tribromophenol). The resultant reaction can be expressed as: $Ph{\cdot}NO{:}N{\cdot}SO_3{\cdot}C_7H_7 + H_2O \longrightarrow Ph{\cdot}OH + N_2 + C_7H_7{\cdot}SO_3H$, but the formation of phenol strongly suggests that a diazonium salt is an intermediate in the hydrolysis. The following experiments, made to test this theory, show beyond doubt that diazo-compounds are produced when azoxysulphones are hydrolysed by either acids or alkalis, and the theoretical implications are dealt with below. (i) Phenyl *p*-tolyl azoxysulphone dissolves smoothly in ice-cold concentrated sulphuric acid; the solution, when diluted with water, exhibits the reactions of benzenediazonium sulphate solution. Diphenyl azoxysulphone, treated similarly, yielded benzenesulphonic acid. (ii) When the azoxysulphone is refluxed with 30% sodium hydroxide, a solution of benzene *iso*diazotate is formed. (iii) When the azoxysulphone is boiled for a few seconds with aqueous-alcoholic alkali containing β-naphthol, a good yield of benzeneazo-β-naphthol is obtained.

From these experiments it seems a possible assumption that the primary product of the hydrolysis of an azoxysulphone is a *n*-diazotate. This then apparently reacts according to the conditions, giving an azo-compound with β-naphthol, an *iso*diazotate with hot concentrated alkali, a diazonium salt with acid, and a phenol with boiling acid.

There has been much discussion about the constitution of *n*-diazotates, much of which has become meaningless in the light of modern theories of valency. It is clear, however, that only two formulæ are now seriously put forward as possible structures for the *n*-diazotate ion, *viz.*, (V) and (VI). Formula (V) forms the basis of a

(V.) $Ar{\cdot}N{:}N{\cdot}O^-$ (VI.) $Ar{\cdot}\underset{\downarrow}{N{:}N^-}O$

modified Hantzsch theory, which regards *n*- and *iso*-diazotates as the *syn*- and *anti*-isomers of the above compound, the correlation between the identity of the isomer and the geometrical configuration being left open. Formula (VI), originally proposed rather speculatively by Bamberger, was later supported (with fresh evidence) by Angeli, who regarded *n*- and *iso*-diazotates as being related in the same way as the two forms of an unsymmetrical azoxy-compound. On this theory, *iso*diazotates are denoted by (V) without reference to geometrical configuration.

The hydrolysis of azoxysulphones to *n*-diazotates and sulphonic acids appears to have a direct bearing on the above question, since a *n*-diazotate of Angeli's structure would be formed if the reaction is regarded as being analogous to the hydrolysis of a sulphonamide; *

$$Ar{\cdot}SO_2{\cdot}NR_2 + H_2O \longrightarrow Ar{\cdot}SO_3H + NHR_2$$
$$Ar{\cdot}SO_2{\cdot}N{:}NO{\cdot}Ar' + H_2O \longrightarrow Ar{\cdot}SO_3H + (Ar'{\cdot}NO{:}N)^- + H^+$$

* It has been suggested that azoxysulphones may undergo hydrolysis in the acid solution to aryl*iso*nitroamine $[Ar{\cdot}\underset{\downarrow}{N{:}N}O]H$ and a sulphinic acid, and that these may then interact to form a sulphonic acid and $[Ar{\cdot}\underset{\downarrow}{N{:}N}O]H$ or $[Ar{\cdot}\underset{\downarrow}{N{:}N}]H$. The investigation of this suggestion is a matter of considerable experimental difficulty, but it should be noted that the existing evidence is against it. First, Bamberger (*Ber.*, 1894, **27**, 1554; 1909, **42**, 1682) showed that

It is not claimed, however, that this constitutes in any sense a proof of Angeli's theory. On the contrary, it is recognised that the hydrolysis of azoxysulphones is a further example of an apparently general reaction. Thus, Angeli (*Gazzetta*, 1917, **47**, I, 215) and Pieroni (*ibid.*, 1922, **52**, II, 32) showed that benzeneazoxycarboxyamide (VII, X = $NH_2$) is readily hydrolysed (probably *via* the unstable carboxylic acid) by dilute alkali to

give a *n*-diazotate, to which Angeli therefore ascribed formula (VI). The question is confused by the assertion of Pieroni and Giannini (*ibid.*, 1924, **54**, I, 162) that the closely-related benzeneazoxycarboxylic ester (VII, X = OEt) gave nitrobenzene and ammonia when hydrolysed by dilute alkali (though hydrolysis in the presence of β-naphthol gave benzeneazo-β-naphthol). These products have never been observed in the decomposition of a *n*-diazotate, so that it is easy to suppose, as did Hantzsch and Strasser (*Ber.*, 1931, **64**, 655), that the intermediate (VI), though showing the coupling reaction, is not a *n*-diazotate. Angeli's amides, however, like our azoxysulphones, do not give nitrobenzene and ammonia on hydrolysis; and a critical examination of Pieroni and Giannini's paper (*loc. cit.*) shows that their evidence is incomplete in many important respects. The azoxyesters were obtained as yellow oils which were inadequately purified, characterised, and analysed, and the prior presence in them of the nitro-compounds supposed to be obtained on hydrolysis cannot with certainty be excluded; thus the formation of benzeneazoxycarboxylic ester by oxidation of the azo-compound did not proceed smoothly but led also to azoxybenzene and benzoic acid, and Angeli (*Gazzetta*, 1917, **47**, I, 215) observed that nitrobenzene was a by-product of his oxidation of benzeneazocarboxyamide to the azoxy-compound.

If it is accepted that the products of hydrolysis of all these azoxy-compounds are true *n*-diazotates, either these must be denoted by the Angeli formula (VI), or a transfer of oxygen from one nitrogen atom to the other must be postulated, giving a *n*-diazotate of formula (V). There is neither analogy nor experimental support for this migration, but in any recognition of the Angeli theory recourse must be made to such a transfer in the explanation of, *e.g.*, the facile oxidation of *n*-diazotates to arylnitroamines. On either Hantzsch's or Angeli's theory, therefore, acceptance of oxygen transfer is essential, and since one of the chief drawbacks to the latter hypothesis has always been this very migration, it seems that Angeli's theory merits more serious consideration than it has yet received outside his own circle. It must be admitted, however, that the hydrolysis of azoxysulphones raises, rather than solves, problems, and no pronouncement can yet be made on the structure of the *n*-diazotates.

## Experimental.

*Diphenyl Azoxysulphone* (III, Ar = Ar′ = Ph).—Nitrosobenzene (0·8 g.) and chloramine-B (2·1 g.) were mixed in pyridine (14 c.c.) and left at room temperature overnight; the reaction was completed by heating on the water-bath (80°) for 2 hours. The liquid was then diluted with water (100 c.c.), and the pale brown crystals (1·6 g.; 82%) collected. After two recrystallisations from 95% alcohol, in which it is rather sparingly soluble, *diphenyl azoxysulphone* formed very pale yellow needles, m. p. 123°, readily soluble in acetone and benzene (Found: C, 54·5; H, 4·0; N, 10·8; *M*, modified Rast using *s*.-tribromophenol, 272. $C_{12}H_{10}O_3N_2S$ requires C, 54·9; H, 3·9; N, 10·7%; *M*, 262).

*Phenyl* p-*Tolyl Azoxysulphone* (III; Ar = Ph, Ar′ = p-$MeC_6H_4$).—A mixture of nitrosobenzene (1 g.) and chloramine-T (3 g.) in pyridine (10 c.c.) was kept overnight and then heated for 2 hours at 80°. On dilution with water (30 c.c.), an oil separated, which rapidly crystallised. After refrigeration, nearly pure *azoxysulphone* (2·3 g.; 92%) was collected, m. p. 109—111°. Recrystallisation from 95% alcohol gave very pale yellow needles, m. p. 112—113°, very soluble in cold benzene, chloroform, and acetone, moderately in ether and hot alcohol, insoluble in water and light petroleum (Found: C, 56·5; H, 4·9; N, 10·3; S, 11·8; *M*, modified Rast, 254. $C_{13}H_{12}O_3N_2S$ requires C, 56·5; H, 4·4; N, 10·2; S, 11·6%; *M*, 276).

The following substances were made by similar methods, all crystallisations being from 95% alcohol:—

| Azoxysulphone. | Description. | M. p. | Yield, %. | N, %. Found. | N, %. Reqd. | *M*. Found. | *M*. Reqd. |
|---|---|---|---|---|---|---|---|
| o-*Tolyl* p-*Tolyl* ..... | Pale yellow prisms | 82° | 56 | 9·8 | 9·7 | 277 | 290 |
| *Di*-p-*tolyl* ..... | Pale yellow plates | 106 | 65 | 9·8 | 9·7 | 300 | 290 |
| m-*Nitrophenyl* p-*Tolyl* ..... | Very pale yellow needles | 122·5—124 | 87 | 13·2 | 13·1 | — | — |
| p-*Phenetyl* p-*Tolyl* ..... | Bright yellow needles | 128—128·5 | 63 | 8·8 | 8·8 | — | — |

p-*Dimethylaminophenyl* p-*Tolyl Azoxysulphone* (III; Ar = *p*-$NMe_2{\cdot}C_6H_4$, Ar′ = *p*-$C_6H_4Me$).—A mixture of *p*-nitrosodimethylaniline (4·8 g.) and chloramine-T (9·0 g.) was left at room temperature in pyridine (60 c.c.) for 24 hours. It was diluted to *ca.* 350 c.c. with water, and the clear deep-red solution refrigerated overnight, giving a crop of large, dark red needles (8 g., 80%). Subsequent dilution gave a further small, tarry crop. The *azoxysulphone*, recrystallised twice from benzene and once from absolute alcohol, formed reddish-purple prisms, m. p. 182° (decomp.) (Found: C, 56·4; H, 5·4; N, 13·1; S, 10·4. $C_{15}H_{17}O_3N_3S$ requires C, 56·4; H, 5·3; N, 13·1; S, 10·1%). This azoxysulphone can be recrystallised from benzene or glacial acetic acid; it is moderately soluble in cold acetone and hot alcohol, but insoluble in light petroleum. It is a very weak base; boiling 2N-sulphuric acid dissolves it slightly, giving a pink solution, but warm concentrated hydrochloric acid dissolves it easily to a colourless solution, from which the free base is precipitated in crystalline form on dilution.

---

phenyl*iso*nitroamine is instantaneously decomposed by mineral acid; in the present instance, therefore, an important competition factor in rates of reaction would come into play. Secondly, Bamberger (*Ber.*, 1898, **31**, 582) showed that alkaline reduction of phenyl*iso*nitroamine yields an *iso*diazotate, whereas it is shown in this communication that dilute alkaline hydrolysis of azoxysulphones gives a *normal* diazotate. In the absence of other evidence, therefore, it would seem to be correct to regard the hydrolysis of azoxysulphones as resulting in the formation of *n*-diazotates and sulphonic acids.

The following substances were made by similar methods, crystallisations being carried out in absolute alcohol:

| Azoxysulphone. | Description. | M. p. | Yield, %. | N, %. Found. | N, %. Reqd. | S, %. Found. | S, %. Reqd. |
|---|---|---|---|---|---|---|---|
| p-*Dimethylaminophenyl Phenyl*..... | Bronze needles | 175—176° | 15* | 13·4 | 13·7 | 10·7 | 10·5 |
| p-*Diethylaminophenyl* p-*Tolyl* ..... | Bright red needles | 178—179 | 51 | 11·9 | 12·1 | 9·6 | 9·2 |

* Early experiment, not repeated.

m-*Phenylene Bis*-(p-*tolyl Azoxysulphone*) (VIII).—*m*-Dinitrosobenzene (0·2 g.) and chloramine-T (0·85 g.) were heated in pyridine (3 c.c.) at 80° for 4 hours. After dilution with water, the yellow solid was collected and washed with hot alcohol. The *bis-azoxysulphone* separated from glacial acetic acid (50% yield) in curious, lens-shaped, pale yellow crystals, m. p. 208° (decomp.) after darkening above 200°. It is rather sparingly soluble in low-boiling organic solvents (Found: N, 11·5. $C_{20}H_{18}O_6N_4S_2$ requires N, 11·4%).

*Reduction of Phenyl* p-*Tolyl Azoxysulphone.*—The azoxysulphone (1 g.) was dissolved in boiling alcohol (10 c.c.) containing glacial acetic acid (1 c.c.). Zinc dust was cautiously added, and when the initial violent reaction had subsided the colourless solution was filtered. The filtrate, on dilution with very dilute hydrochloric acid, gave nearly pure *p*-toluenesulphonylphenylhydrazide (0·61 g., 64%), m. p. 154° (decomp.). A mixture with an authentic specimen (m. p. 156°, decomp.) melted at 153—156° (decomp.).

*Hydrolyses of Phenyl* p-*Tolyl Azoxysulphone.*—(i) The azoxysulphone (0·5 g.) was distilled with 50% sulphuric acid (60 c.c.), soon forming a pale bluish-purple solution. Phenol could be detected in the distillate by its odour, and was converted into 2 : 4 : 6-tribromophenol (51% yield), m. p. 90—92°, mixed m. p. 91—93°.

(ii) The azoxysulphone (0·4 g.) was added in portions to concentrated sulphuric acid (2 c.c.) cooled in an ice-bath, the temperature being kept below 10°. Five minutes after all the crystals had dissolved, the liquid was poured into ice-water (40 c.c.). The clear solution, when poured into excess of an alkaline solution of β-naphthol, gave quantitatively (0·355 g.) nearly pure benzeneazo-β-naphthol, identified by mixed m. p.

(iii) The azoxysulphone (0·5 g.) and β-naphthol (0·25 g.) were dissolved in boiling 95% alcohol (5 c.c.) containing a few drops of 30% sodium hydroxide. A blood-red colour developed; after boiling for 2 mins. the liquid was diluted with water, and the crude azo-compound collected. One recrystallisation from alcohol gave pure benzene azo-β-naphthol, m. p. 130° (0·30 g., or 67%), identified by mixed m. p.

(iv) The azoxysulphone (0·56 g.) was refluxed with 30% sodium hydroxide (15 c.c.) for 30 mins.; frothing then became uncontrollable, and the mixture was cooled, diluted, and filtered. The residue consisted of a red solid (0·26 g.), which was recrystallised from a little alcohol, giving unchanged azoxysulphone (0·16 g., 29%). The red compound present in the alcoholic mother-liquors could not be isolated. The filtrate coupled very slowly with β-naphthol in the cold (pink colour on standing overnight), but when it was acidified, and again made alkaline, coupling was immediate. The *iso*-diazotate was estimated by acidifying and coupling with an alkaline solution of 2-hydroxy-3-naphthoic anilide; the yield of azo-dye was 0·44 g. (59%).

*Hydrolysis of Diphenyl Azoxysulphone.*—The azoxysulphone (0·3 g.) was dissolved in concentrated sulphuric acid (3 c.c.) at 0°, and after 30 minutes the solution was poured into ice-water, boiled to decompose the diazonium salt, and neutralised with calcium carbonate. The calcium sulphate was collected and washed with water, and the combined filtrate and washings were made faintly acid with hydrochloric acid and freed from sulphate ions with barium chloride. The filtered solution was concentrated to about 10 c.c., mixed with an equal volume of a saturated solution of β-naphthylamine hydrochloride, and cooled to 0°. β-Naphthylamine benzenesulphonate (0·22 g., 64%) (Keyworth, *J. Soc. Chem. Ind.*, 1924, **43**, 341T) separated in colourless plates, m. p. 244° (corr.), of which the identity was confirmed by mixed m. p. with an authentic sample.

Our thanks are due to Mr. J. E. Still for carrying out the micro-analyses, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (W. V. F.).

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February 22nd,* 1944.]

## 99. *The Reaction between Amines and Unsaturated Compounds containing Halogen attached to one of the Ethylenic Carbon Atoms. Part III. The Influence of a* gem-*Dimethyl Group.*

By HARRY C. MURFITT and JOHN C. ROBERTS.

Reactions similar to those reported in Part II (J., 1938, 963) have been investigated. The presence of a *gem*-dimethyl group on the β-carbon atom leads to simple replacement of the halogen by the amine as the main reaction; apparently some simultaneous addition of the amine to the double bond also occurs.

IT has previously been shown by one of us (Parts I and II, J., 1936, 1169; 1938, 963) that compounds of the type $CHR{:}CX{\cdot}CO_2Et$ (X = halogen; R = Me or Ph) react readily with strongly basic secondary amines to yield αβ-diamines. It is now shown that ethyl α-bromoacrylate (X = Br; R = H) reacts similarly. However, ethyl α-bromo-ββ-dimethylacrylate reacted with piperidine to yield mainly ethyl α-piperidino-ββ-dimethylacrylate, isolated and identified as the *platinichloride*; the pure free base was not obtained. The rate of production of ionisable bromine was comparatively slow. Dimethylamine reacted similarly, ethyl α-dimethylamino-ββ-dimethylacrylate being isolated as its *hydrochloride*. In both instances analysis of the basic initial product indicated contamination with some other substance of higher nitrogen content which we believe to be the corresponding diamine. Attempts to separate the free bases by fractional distillation in a vacuum were unsuccessful.

The presence of the *gem*-dimethyl group on the β-carbon atom thus diminishes the reactivity of the ester towards the addition of the amine across the double bond. This is undoubtedly due to the marked electron-release capacity of the *gem*-dimethyl group which will render the double bond less liable to attack by the

nucleophilic reagent. It is significant that ββ-dimethylacrylic acid shows an enhanced reactivity (compared with other αβ-unsaturated acids) towards the addition of bromine—an electrophilic reagent (Sudborough and Thomas, J., 1910, **97**, 2450; Anantakrishnan and Venkataraman, *Chem. Reviews*, 1943, **33**, 44).

## Experimental.

*Ethyl α-Bromoacrylate.*—The pure ester has apparently never been prepared. Of three different methods of preparation investigated, Michael's modification (*Amer. Chem. J.*, 1887, **9**, 121) of Wagner and Tollens's method (*Annalen*, 1874, **171**, 350) yielded the purest product. From silver α-bromoacrylate (5 g.) and ethyl bromide (8 c.c.) were obtained 1·25 g. of crude ester, which was dried (sodium sulphate) and distilled in a vacuum, Pregl's micro-apparatus being used. Ethyl α-bromoacrylate (0·75 g.) was obtained as a colourless oil, b. p. 63·5—65°/15 mm. (Found: Br, 45·8. Calc. for $C_5H_7O_2Br$: Br, 44·7%). Only small quantities were prepared at one time, since on storage for a few days, even in a sealed container and in the dark, the ester turned into a glass.

*Reaction between Ethyl α-Bromoacrylate and Dimethylamine.*—(i) 0·136 G. of the ester was treated with 0·31 g. of a 33% solution of dimethylamine (3 mols.) in absolute alcohol. Heat was evolved and colourless crystals separated. After ¼ hour, water and an excess of dilute nitric acid were added; titration with 0·1N-silver nitrate indicated that 99·6% of the bromine had been removed from the ester.

(ii) 1·38 G. of dimethylamine (3 mols.) solution were added slowly to 0·61 g. of the ester; the mixture was cooled in ice when necessary and then kept for 1 hour. The basic product (about 0·2 c.c.), isolated in the usual way (similar to that for the isolation of ethyl αβ-dipiperidinobutyrate, Part II), yielded a picrate (from alcohol) identical (crystalline form, m. p. and mixed m. p.) with that of ethyl αβ-bis(dimethylamino)propionate. The free base was more conveniently prepared on a larger scale from ethyl αβ-dibromopropionate (see below).

*Reaction between Ethyl α-Bromoacrylate and Piperidine.*—0·172 G. of the ester was treated with 0·89 c.c. of a solution of piperidine (0·245 g., 3 mols.) in absolute alcohol. Much heat was evolved and a little white colloidal matter separated. After ½ hour 79·3% of the bromine had been removed from the ester.

*Ethyl αβ-Bis(dimethylamino)propionate.*—40 G. of αβ-dibromopropionic acid, esterified with alcoholic hydrogen chloride, yielded the ethyl ester (32·5 g.), b. p. 215—218°/757 mm. (Münder and Tollens, *Annalen*, 1873, **167**, 230, give b. p. 211—214°/746 mm.). This ester, on treatment with dimethylamine (4 mols.) solution, yielded 96·2% of the bromine in an ionisable state after ¾ hour. Dimethylamine (4 mols.) solution was added gradually and with cooling to 15·2 g. of ethyl αβ-dibromopropionate. After ¾ hour, the basic product (2·2 g., yield 20%) was isolated in the usual manner, but with a reduction in the volume of water since the product is water-soluble. *Ethyl αβ-bis(dimethylamino)propionate* was obtained as a colourless oil of unpleasant basic odour, b. p. 95—96°/14 mm., very easily soluble in water (Found: C, 57·1; H, 10·8; N, 14·7. $C_9H_{20}O_2N_2$ requires C, 57·4; H, 10·6; N, 14·9%). The *picrate* separated from alcohol in yellow prisms, m. p. 122—123° (decomp.) (Found: N, 17·2. $C_9H_{20}O_2N_2,2C_6H_3O_7N_3$ requires N, 17·3%). The *platinichloride* crystallised in small orange-coloured cubes which started to decompose at 186° and melted (decomp.) at 190° (Found: Pt, 32·3. $C_9H_{20}O_2N_2,H_2PtCl_6$ requires Pt, 32·6%).

*Ethyl αβ-Dipiperidinopropionate.*—13·7 G. of piperidine (4 mols.), dissolved in absolute alcohol (30 c.c.), were added dropwise and with shaking to ethyl αβ-dibromopropionate (10·5 g.) immersed in crushed ice. During the addition the mixture was kept as near 0° as possible and was afterwards left overnight at room temperature. Addition of water (200 c.c.) and sodium chloride (50 g.)—the latter to increase the density of the aqueous phase—caused a pale yellow oil to float on the surface. The oil was removed and treated with crushed ice and an excess of dilute hydrochloric acid to dissolve the basic ester. The solution was then purified, and the product (3·84 g., 36%) isolated in the usual way. *Ethyl αβ-dipiperidinopropionate* was obtained as a colourless viscous oil of basic unpleasant odour, b. p. 175—176·5°/13 mm., insoluble in water (Found: C, 67·2; H, 10·1; N, 10·7. $C_{15}H_{28}O_2N_2$ requires C, 67·2; H, 10·5, N, 10·5%). A crystalline picrate could not be obtained.

*Ethyl α-Bromo-ββ-dimethylacrylate.*—Of two different methods of preparation which were investigated, the following proved the more satisfactory:

$$CMe_2{:}CH{\cdot}CO_2H \xrightarrow[HCl]{EtOH} CMe_2{:}CH{\cdot}CO_2Et \xrightarrow{Br_2} CMe_2Br{\cdot}CHBr{\cdot}CO_2Et \xrightarrow{EtONa} CMe_2{:}CBr{\cdot}CO_2Et$$

90 G. of bromine (1·06 mols.), dissolved in carbon tetrachloride (50 c.c.), were slowly added in the cold to 68 g. of ethyl ββ-dimethylacrylate in carbon tetrachloride (250 c.c.); the reaction mixture was protected from light. After standing for a few days, the excess of bromine and the carbon tetrachloride were distilled from a water-bath, and the residue distilled in a vacuum, yielding ethyl αβ-dibromo*iso*valerate (133 g.), b. p. 112—114°/18 mm. (Prentice, *Annalen*, 1896, **292**, 273, gives b. p. 127—128°/30 mm.). The dibromo-ester (133 g.) was treated with a solution of sodium ethoxide prepared from sodium (10·6 g., 1 atom) and absolute alcohol (283 c.c.). The sodium bromide was removed by filtration, and the alcohol distilled off; the residue was dissolved in ether, washed with water, dried (calcium chloride), the solvent evaporated, and the residue distilled in a vacuum, yielding 76·5 g. of *ethyl α-bromo-ββ-dimethylacrylate*, b. p. 88—89°/13 mm. (Found: C, 40·1; H, 5·7; Br, 38·3. $C_7H_{11}O_2Br$ requires C, 40·6; H, 5·4; Br, 38·6%).

*Reaction between Ethyl α-Bromo-ββ-dimethylacrylate and Piperidine.*—Small-scale experiments, carried out as before, with 1 mol. of ester and 3 mols. of piperidine in absolute alcohol yielded the following results:

| Time of reaction, hours | ½ | 2 | 3 | 4 | 48 |
|---|---|---|---|---|---|
| Bromine replaced, % | 11 | 17 | 23 | 30 | 82 |

20 G. of ethyl α-bromo-ββ-dimethylacrylate were treated with 28·1 c.c. of piperidine (3 mols.) dissolved in 32·3 c.c. of alcohol (95%), and the mixture kept at room temperature for 3 days. Isolation of the basic product by the usual method gave a pale yellow oil (12·5 g.), b. p. 130—134°/20 mm. Refractionation yielded a colourless oil, b. p. 121—123°/17 mm. (Found: N, 7·1. Calc. for the monopiperidino-ester: N, 6·6. Calc. for the dipiperidino-ester: N, 9·5%). On treatment of ethyl α-bromo-ββ-dimethylacrylate with alcoholic piperidine (2 mols.) a product was obtained of b. p. 122—124°/18 mm. (Found: N, 7·0%). This did not afford a crystalline picrate, but with platinichloric acid, it gave orange-coloured crystals with yellow wart-like incrustations; two recrystallisations from small quantities of alcohol (80%) yielded the pure *platinichloride* of ethyl α-piperidino-ββ-dimethylacrylate as orange-coloured, square platelets, which sintered at 179° and melted at 183° (decomp.) (Found: C, 34·6; H, 5·4; N, 3·2; Pt, 23·5. $2C_{12}H_{21}O_2N,H_2PtCl_6$ requires C, 34·6; H, 5·3; N, 3·4; Pt, 23·4%).

*Reaction between Ethyl α-Bromo-ββ-dimethylacrylate and Dimethylamine.*—Speed of reaction:

| Time of reaction, hours | ½ | 1½ | 3½ | 18 | 24 | 68 |
|---|---|---|---|---|---|---|
| Bromine replaced, % | 15 | 21 | 30 | 60 | 72 | 93 |

12·6 G. of ethyl α-bromo-ββ-dimethylacrylate were treated with 31·5 g. of 26% dimethylamine (3 mols.) solution in alcohol and left at room temperature for 3 days. The usual method of isolation yielded an oil (3·2 g.), b. p. 76—78°/

18 mm. [Found : N, 8·8. Calc., for the dimethylamino-ester : N, 8·2. Calc., for the bis(dimethylamino)-ester : N, 13·0%]. No platinichloride or picrate could be obtained, but when 2·3 g. of the crude base were dissolved in absolute alcohol (2 c.c.) and mixed with 4 c.c. of a 10·1% (w/v) solution of hydrogen chloride (1 equiv.) in absolute alcohol, and the mixture was diluted with dry ether (150 c.c.), the viscous oily *hydrochloride* of ethyl α-dimethylamino-ββ-dimethylacrylate separated. This was washed with a little dry ether and dried in a vacuum over phosphoric oxide, and after some weeks a very deliquescent white powder was formed (Found : Cl, 14·7. $C_9H_{17}O_2N,HCl$ requires Cl, 14·4%).

We wish to record our thanks to Mr. J. E. Still for a number of micro-analyses, and to the Chemical Society for a grant.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, May 9th*, 1944.]

---

## 100. *The Metal-catalysed Reaction between Acetylene and Hydrogen. Part I. Nickel Catalysts.*

By J. SHERIDAN.

The rate of fall in total pressure in hydrogen–acetylene mixtures over nickel–pumice catalysts increases, under constant conditions, during the early stages of use of the catalysts. The yields of ethylene, ethane, and higher hydrocarbons, expressed in terms of the acetylene not recovered, are the same on fresh and old catalysts. The course of reaction in 1 : 1 and 2 : 1 hydrogen : acetylene mixtures on catalysts of constant activity is plotted. Ethylene is produced at about 5 times the rate of ethane formation until most of the acetylene is removed. The products other than $C_2$ hydrocarbons have an empirical gross composition of about $C_4H_7$, and are formed in yields of 55—60% of the acetylene not recovered at all stages of reaction, with both gas ratios. The initial reaction on catalysts of constant activity is of first order with respect to hydrogen and of approximately zero order with respect to acetylene. The hydrogenation to ethylene and the formation of reduced polymers of acetylene both have kinetics of approximately this type, but differing slightly such that an increase from 1 : 8 to 8 : 1 in initial hydrogen : acetylene ratio causes an increase from about 40% to 67% in the yield of $C_2$ hydrocarbons, expressed in terms of the acetylene not recovered. Ethylene added to the system acts principally as an inert diluent, and is apparently less strongly adsorbed than acetylene on nickel. The same catalysts have negligible action on acetylene alone under conditions of rapid reaction in acetylene–hydrogen mixtures. The results are discussed with special reference to previous work on the chemisorption of ethylene and acetylene.

IT has long been known that the reduction of acetylene by hydrogen in the presence of metal catalysts is not normally a quantitative hydrogenation to ethylene and ethane, but is accompanied by the formation of reduced polymers of acetylene under almost all conditions. It is remarkable that the latter process usually takes place at temperatures well below those at which the metals have any appreciable effect on acetylene alone. Previous work has been principally of a qualitative nature, and a systematic study of the kinetics of the reaction on various catalysts appeared desirable, with special attention to the analysis of the products. Such a study has accordingly been made with a number of metals under varied conditions of temperature and partial pressures of reactants. In the present communication an account is given of the kinetics of the reaction in the presence of nickel.

Sabatier and Senderens (*Compt. rend.*, 1899, **128**, 1173) found that acetylene and hydrogen reacted over nickel to give ethylene, ethane, and higher hydrocarbons. Later workers have reported widely varying yields of these products (Ross, Culbertson, and Parsons, *Ind. Eng. Chem.*, 1921, **13**, 775; Yoshikawa, *Bull. Chem. Soc. Japan*, 1932, **7**, 201; Pichler, *Ges. Abh. Kennt. Kohle*, 1934, **11**, 395; Ackermann, *Brennstoff-Chem.*, 1937, **18**, 357; Fischer and Peters, *ibid.*, 1931, **12**, 286; Petrov and Antsus, *J. Appl. Chem. U.S.S.R.*, 1933, **6**, 1145; Dupont, *Bull. Soc. chim.*, 1936, **3**, 1030; Dupont and Lombard, *ibid.*, 1941, **8**, 851; see also U.S.P. 1,392,852, 1921; B.P. 336,999, 1929). The differences among the results of these investigators are to be traced partly to differences in the conditions of reaction and partly to difficulties in controlling the flow methods almost always employed. There has been no previous investigation of the kinetics of the reaction, and very little systematic study of influences of conditions on the products. The reduced polymers of acetylene formed are principally aliphatic, and cover a wide range of molecular weights from the $C_4$ series upwards, but the literature provides little detailed knowledge of their structure (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, **4**, 445; *Compt. rend.*, 1902, **134**, 1185; Charitschkow, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 880; Oda, *J. Chem. Ind. Japan*, 1921, **24**, 1161; Binnie, *Chem. and Ind.*, 1931, **50**, 297; Petrov and Antsus, *loc. cit.*; *Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **4**, 300; *Refiner Natural Gasoline Manfr.*, 1934, **13**, 79; Russian Patent 49,724, 1936; *J. Physical Chem. U.S.S.R.*, 1940, **14**, 1308; *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.*, 1940, 274).

The present research aimed at more detailed and systematic investigation, especially of the kinetics of the reaction, for which purpose use has been made of the greater control afforded by a static reaction system. The complexity of the reaction has demanded frequent full analysis of the gaseous products. An investigation of some of the reduced polymers of acetylene formed has also been carried out, and will be reported later.

### EXPERIMENTAL.

*Acetylene.*—Cylinder gas was passed in succession through the following solutions : chromic acid, 10% mercuric chloride in dilute hydrochloric acid, sodium hydrosulphite, sodium bisulphite (two wash bottles), 20% sodium hydroxide. It was dried by passage through a U-tube containing anhydrous calcium chloride. Periodic analyses by the methods described below showed a minimum acetylene content of 99·5%, with about 0·2% of other unsaturated hydrocarbons. Small amounts of hydrogen and nitrogen were probably present. No attempt was made to remove the very last traces of oxygen; if it was present, its amount was less than 0·1%.

*Hydrogen.*—Electrolytic cylinder gas was used. The minimum hydrogen content was 99·5%, with about 0·1% each of carbon monoxide and dioxide. No oxygen was detected by pyrogallol absorption.

*Ethylene.*—Cylinder gas, about 99% pure and containing traces of air, was used without further treatment.

*Catalysts.*—Pumice granules, 2—5 mm. in diameter, were used as carrier substance. They were cleaned by boiling with concentrated hydrochloric acid, and had no measurable action on acetylene alone or mixed with hydrogen, at 358°. The catalysts used in the present experiments, designated as Ni-1 and Ni-2, had nickel : pumice ratios of 1 : 10 and 1 : 5 by weight respectively. They were prepared by evaporation of solutions of nickel nitrate containing pumice, ignition in an open dish till decomposition was nearly complete, followed by reduction in hydrogen containing ethanol vapour at 400—425° for 2 hours.

*Apparatus.*—Experiments were performed in a static system at constant volume. The Pyrex reaction bulb (300 c.c.) with capillary leads (capacity about 2 c.c.) formed part of an all-glass system, consisting in addition of gas-storage vessels, a McLeod gauge, and a mercury-vapour pump and oil pump in series. The bulb was surrounded by steel turnings and metal screens inside a heavily lagged furnace. Temperature (20—170°) was controlled by a sealed mercury-in-glass thermometer regulator. Even in experiments lasting several hours temperatures did not vary by more than 0·5° from the stated value. Gases were admitted in succession to the bulb, pressure being measured on a mercury capillary manometer. In most experiments hydrogen was admitted first. Gas was withdrawn from the bulb at selected times into a mercury-filled gas burette. Error due to a dead space in the capillary leads was reduced by withdrawing and rejecting about 2 c.c. of gas some 30 secs. before the collection.

The weight of catalyst placed in the bulb was 2 g.; it was normally heated to 300—350° in 400—500 mm. of hydrogen for several hours before experiments were performed over it, and was not allowed to come into contact with air during the period of its use.

*Analysis of Gaseous Products.*—A Bone and Wheeler apparatus was used. An alkaline solution of mercuric cyanide (Treadwell and Tauber, *Helv. Chim. Acta*, 1919, **2**, 601) proved a satisfactory absorbent for acetylene. Two minutes' shaking with 10 c.c. of this solution sufficed to absorb the acetylene in samples (up to 40 c.c.) containing over 99% of this gas. Ethylene absorption in this reagent was negligible, despite high ethylene contents in many cases. The separate estimation of ethylene and higher unsaturated hydrocarbons was more difficult. Tests showed that all the higher unsaturated hydrocarbons could be absorbed in 10 c.c. of 85% sulphuric acid in 5—10 minutes, but it is probable that traces of ethylene were also taken up, especially when much of this gas was present. In practice, a 7-minute exposure to 85% acid was used (after the acetylene absorption), followed by absorption of the ethylene. The error in ethylene and higher unsaturated contents was probably not more than 1% of the total gas. Other gases were estimated by standard methods.

*Results.*—The analytical figures were usually converted into partial pressures (expressed to the nearest mm.) for comparison with the initial pressures. There were no indications that the adsorption of gases by the catalysts caused appreciable errors in the pressure data. An error of $\pm 2$ mm. seems a reasonable one in most cases, though the uncertainty may be greater in the case of fast reactions. The 1—2% of the final pressures not accounted for in the listed products must be due in part to traces of nitrogen picked up during the gas analysis. No correction has been applied for the possible condensation of less volatile products during the withdrawal of gas for analysis. Condensation was not apparent in the present experiments, and there is no indication that any important correction for it is necessary.

The value of $n$ in $C_nH_{2n+2}$ for the saturated hydrocarbons in the products, after removal of hydrogen, was always very close to 2·0. Since methane production is not likely to be appreciable, it is improbable that compounds higher than ethane were present in large amount. The stated ethane contents are the saturated hydrocarbon contents; the real ethane figures will be slightly less if traces of higher hydrocarbons or methane were present.

Admission of hydrogen first to the evacuated bulb was followed by a fall in pressure of 5—15 mm. in about 10 minutes, except when the catalyst had not previously been used. This was probably due to hydrogenation of non-volatile unsaturated hydrocarbons on the catalyst, and had normally proceeded almost to completion before the pressure was read and taken as the initial pressure of hydrogen.

## Discussion.

(i) *Shape of Pressure–Time Curves.*—A nearly linear pressure–time curve was usually obtained for the first stages of reaction in hydrogen–acetylene mixtures, though in some examples the rate of fall in total pressure increased slightly in the early phase of reaction. This early acceleration was a little more marked at higher temperatures, but was not more pronounced in mixtures rich in hydrogen. In all cases the fall in pressure gradually became slower towards the end of the reaction, with no increase in rate at a late stage such as occurs in hydrogen–acetylene mixtures over platinum (Farkas and Farkas, *J. Amer. Chem. Soc.*, 1939, **61**, 3396) and palladium (Cremer, Knorr, and Plieninger, *Z. Elektrochem.*, 1941, **47**, 737).

(ii) *Ageing of Catalysts.*—The activity of the catalysts, as measured by the rate of fall in total pressure in similar hydrogen–acetylene mixtures at the same temperature, always increased markedly in the early stages of use of the catalysts. For example, with some 300 mm. each of acetylene and hydrogen at 95—96° on a new sample of Ni-2, the initial rates of fall in total pressure were about 5, 14, and 30 mm./min. in that sequence for the first three experiments. The rates at equal falls in pressure were in roughly the same ratio throughout the reactions. The increase in activity occurred even after very long pre-reduction of the nickel (40 hours at 340—370° in 470 mm. of hydrogen). After several experiments in which the reaction ran most of its course, the increase in activity of the catalysts ceased, and their activity towards hydrogen–acetylene mixtures then remained fairly steady for considerable periods. The effects of variations in conditions on the reaction were studied, unless otherwise stated, on catalysts in this state of steady activity.

Since the slight acceleration in the early stages of some experiments persisted after the activity of the catalyst had ceased to increase, the acceleration appears to have a cause other than that leading to the general increase in activity, which is presumably due to some modification of the catalyst surface.

(iii) *Yields of Various Products.*—Table I summarises data for some experiments on new catalysts and on the same catalysts in a used state. Each group of experiments refers to a separate specimen of catalyst, the runs in each group being numbered in the sequence of their performance. Unsaturated hydrocarbons higher than the $C_2$ series accounted for 6—14 mm. of the final pressures. With 209—400 mm. of hydrogen and 199—317 mm. of acetylene at 83—146° the yields, expressed as percentages of the acetylene not recovered, were:

ethylene, 30—39%; ethane, 4—9%; other products, 52—66%. These yields refer to stages of reaction up to the point when the acetylene pressure had fallen to 5 mm. The products other than ethylene and ethane accounted for the removal of rather more acetylene than hydrogen, having an empirical overall composition in the region of $C_4H_7$. Little change in the yields of ethylene, ethane, and other products, or in the composition of the last, accompanied the increase in activity of the catalysts during the first few experiments over them, and this increase is therefore not specifically in favour of a particular type of reaction in the system. In this table $\Delta p$ refers to the fall in pressure (in mm.), and $t$ to the duration of the experiment (in mins.).

TABLE I.

| Catalyst. | No. of expt. in series over each specimen. | Initial pressure (mm.). $H_2$. | Initial pressure (mm.). $C_2H_2$. | Temp. | $\Delta p$. | $t$. | Press., mm., in gaseous product. $C_2H_2$. | $C_2H_4$. | $H_2$. | $C_2H_6$. | Yield (%). $C_2H_4$. | Yield (%). $C_2H_6$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ni-1 | 1 | 221 | 274 | 101° | 295 | 51 | 56 | 69 | 47 | 12 | 32 | 6 |
| | 2 | 209 | 208 | 146 | 296 | 11 | 5 | 66 | 17 | 18 | 33 | 9 |
| | 4 | 224 | 273 | 101 | 297 | 20 | 59 | 76 | 36 | 14 | 35 | 7 |
| | 5 | 217 | 275 | 104 | 292 | 17 | 60 | 75 | 36 | 12 | 35 | 6 |
| | 6 | 221 | 272 | 101 | 293 | 19 | 61 | 72 | 37 | 13 | 34 | 6 |
| Ni-2 | 1 | 301 | 306 | 95 | 412 | 75 | 5 | 105 | 52 | 17 | 35 | 6 |
| | 2 | 300 | 317 | 96 | 348 | 23 | 64 | 96 | 82 | 13 | 38 | 5 |
| | 5 | 295 | 307 | 96 | 344 | 11 | 66 | 73 | 87 | 10 | 30 | 4 |
| | 11 | 307 | 304 | 79 | 342 | 40 | 61 | 86 | 86 | 13 | 36 | 5 |
| | 19 | 303 | 298 | 88 | 338 | 30 | 59 | 82 | 88 | 15 | 34 | 6 |
| Ni-1 | 1 | 400 | 199 | 83 | 200 | 21 | 56 | 56 | 252 | 13 | 39 | 9 |
| | 17 | 400 | 200 | 83 | 200 | 9 | 62 | 51 | 257 | 11 | 37 | 8 |

TABLE II.

| Catalyst. | No. of expt. | Temp. | $C_2H_2$ (mm.). | $\Delta p$. | $t$. | Product, volume %. $C_2H_2$. | $C_mH_n$. | $C_2H_4$. | $H_2$. | $C_2H_6$. |
|---|---|---|---|---|---|---|---|---|---|---|
| Ni-1 | 1 | 207° | 478 | 71 | 27 | 84·0 | 1·4 | 12·4 | 0·3 | — |
| | 2 | 244 | 484 | 107 | 21 | 90·1 | 0·7 | 5·4 | 1·3 | — |
| | 3 | 280 | 483 | 124 | 26 | 87·0 | 1·0 | 4·2 | 4·7 | 2 |
| | 4 | 283 | 492 | 131 | 26 | 86·3 | 0·8 | 4·5 | 5·1 | 2 |
| | 5 | 255 | 486 | 85 | 31 | 90·4 | 0·8 | 3·8 | 2·1 | 1 |

(iv) *Comparison of the Acetylene–Hydrogen Reaction with the Reaction in Acetylene alone over the Same Catalysts.*—In the experiments represented in Table I large amounts of acetylene and hydrogen were converted into products less volatile than $C_2$ hydrocarbons. Under the same conditions of temperature and acetylene pressure over the same specimens of catalyst acetylene alone underwent only very slow change. For instance, with 217 mm. of acetylene at 160° over a specimen of Ni-1 the fall in pressure was 6 mm. in 20 minutes, whereas in the preceding experiment (208 mm. of acetylene, 209 mm. of hydrogen) 119 mm. of acetylene were removed as products less volatile than $C_2$ hydrocarbons in 11 minutes at 146°. Subsequent experiments showed that no deactivation of the catalyst had occurred when the experiment with acetylene alone was performed. Acetylene alone did not react at readily measurable rates over these catalysts until the temperature exceeded about 200°. Table II gives some data obtained under these conditions; the initial pressure of acetylene is given, and $C_mH_n$ represents higher unsaturated hydrocarbons. The activity of the catalyst appeared to be varying somewhat, but the products are consistent with the known catalysis of the decomposition of acetylene into carbon and hydrogen by nickel, followed by reaction of hydrogen with acetylene (see, *e.g.*, Egloff, "Reactions of Pure Hydrocarbons," 1937, p. 429). Some of the acetylene must have been removed as products less volatile than $C_2$ hydrocarbons, but it cannot be said whether this removal is partly by direct polymerisation or only accompanies hydrogenation after decomposition of acetylene has produced hydrogen in the system.

(v) *Course of Reaction in Hydrogen–Acetylene Mixtures at Constant Volume over Catalysts of Steady Activity.*—This was determined by performing runs of different durations over the same specimen of catalyst, under constant conditions of temperature and partial pressures of gas. The pressure–time curves were reproducible within fairly narrow limits, but greater consistency of the results was obtained by plotting the data obtained from the gas analysis at time co-ordinates corresponding to the same fall in total pressure in the longest experiment. These times differed from the actual duration of the experiments to an extent determined by the deviations of the total pressure curves from that of the longest experiment. Figs. 1 and 2 show the results for 1 : 1 and 2 : 1 hydrogen : acetylene mixtures at 79° and 72° respectively. The sequence of performance was not related to the duration of the runs, as can be seen from Tables III and IV, which also show the yields of ethylene and

TABLE III.

Yields at different stages in reaction in 1 : 1 $H_2$ : $C_2H_2$ mixture (Catalyst Ni-2, runs 7—18 on the same specimen; see Fig. 1).

| Expt. no. | 17 | 9 | 8 | 10 | 11 | 12 | 7 | 15 | 14 | 16 | 13 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Duration (mins.) | 5 | 10 | 18 | 30 | 40 | 50 | 60 | 74 | 90 | 104 | 120 | 180 |
| Yield of $C_2H_4$, % | 36 | 37 | 34 | 36 | 36 | 36 | 33 | 35 | 35 | 35 | 35 | 33 |
| Yield of $C_2H_6$, % | — | — | 5 | 6 | 5 | 7 | 6 | 7 | 8 | 8 | 7 | 11 |

TABLE IV.

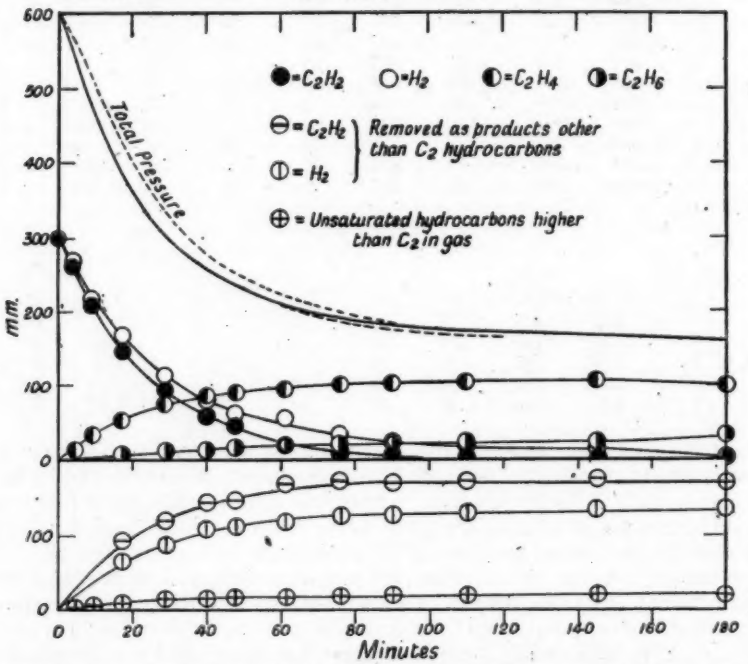
Yields at different stages in reaction in 2 : 1 $H_2 : C_2H_2$ mixture (Catalyst Ni-2; runs 8, 9, 11, and 12 on same specimen; see Fig. 2).

| Experiment no. | 11 | 8 | 12 | 9 |
|---|---|---|---|---|
| Duration (mins.) | 10 | 25 | 40 | 55 |
| Yield of $C_2H_4$, % | 36 | 37 | 34 | 25 |
| Yield of $C_2H_6$, % | 7 | 7 | 11 | 19 |

ethane at each stage, expressed as percentages of the acetylene not recovered. The narrow range within which the total pressure curves were reproducible, and the smooth curves for partial pressures, etc., leave little doubt that reactions represented by the longest total pressure curves follow the courses shown.

FIG. 1.

*Course of reaction in* 1 : 1 $H_2 : C_2H_2$ *mixture at* 79° *over catalyst* Ni-2.




*Initial* $H_2$ *pressure* = 299—307 *mm. Initial* $C_2H_2$ *pressure* = 297—306 *mm.*

*The continuous total-pressure curve is that for the experiment of* 180 *minutes' duration. The dotted lines show the extremes of deviation of the other total-pressure curves from the continuous line.*

In the early stages acetylene was removed a little more rapidly than hydrogen, and ethylene formation was about five times as fast as ethane production. The total yield of ethylene and ethane was 40—45% of the unrecovered acetylene at all stages of reaction and for both gas ratios. The products other than ethylene and ethane had an empirical overall composition of about $C_4H_7$ at all stages. The pressure of unsaturated hydrocarbons higher than the $C_2$ series rose in proportion to the amounts of acetylene and hydrogen removed as products other than $C_2$ hydrocarbons. Ethane production increased, notably in the case of the 2 : 1 gas ratio, when almost all the acetylene had been removed and some hydrogen remained. The ethylene pressure passed through a maximum on account of this effect. The rate of ethylene hydrogenation in the 2 : 1 mixture when the acetylene had been removed was slow compared with the original acetylene–hydrogen reaction.

(vi) *Kinetics of Reaction in Hydrogen–Acetylene Mixtures.*—Fig. 3 shows the effect of variations in partial pressures of acetylene and hydrogen on the initial rate of fall in total pressure over a catalyst of constant activity. The pressure–time curves were almost linear initially, and $(dp/dt)_0$ was taken as the mean rate for the first 15—40 mm. of fall. A fast initial fall of some 2 mm. at high acetylene pressures (admitted after hydrogen) was presumably due to adsorption of acetylene, and the initial rates recorded were the rates in the period of linear fall in pressure which followed. The experiments were performed in a sequence in no way related to the changes in partial pressures, and the rates were reproducible within reasonable limits.

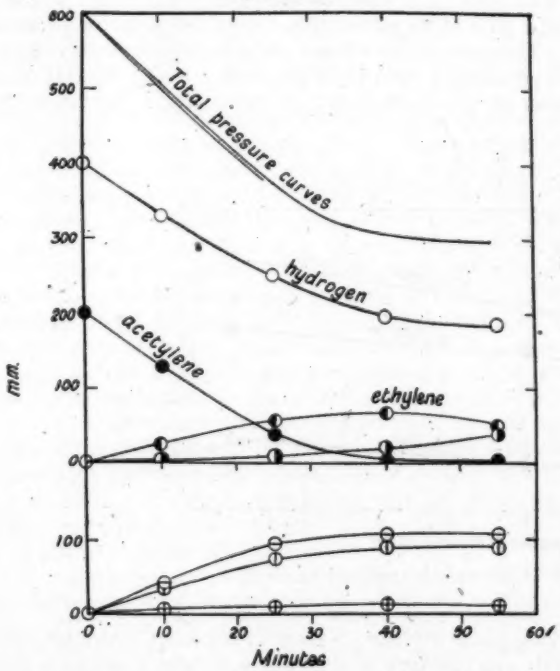
The initial rate was directly proportional to the hydrogen pressure. It appears to be independent, within the limits of error, of the acetylene pressure, though possibly it increased slightly as the acetylene pressure was lowered.

By analysis after falls in pressure of 15—50 mm. figures were obtained for the mean rates of formation of

ethylene and of removal of hydrogen and acetylene in the early reaction. Ethane production was very slight. The linear course of fall in total pressure with time suggests that these mean rates may be taken as the initial rates of the processes concerned. The rate of ethylene production was always about a quarter of the initial rate of fall in total pressure. The rates of removal of acetylene and hydrogen were equal within the error of measurement, and were about two-thirds of the initial rate of fall in total pressure in all cases. The ratio of ethylene formation to acetylene (and hydrogen) removal was thus approximately 3 : 8, which is about the ratio made probable by the data in Figs. 1 and 2. No change in this ratio within the limits of conditions represented by Fig. 3 could be demonstrated. The relationships between the total and the partial initial rates in a given experiment were the same when the catalyst was still increasing in activity, which is in harmony with the fact that the yields are not dependent on the activity of the nickel.

FIG. 2.

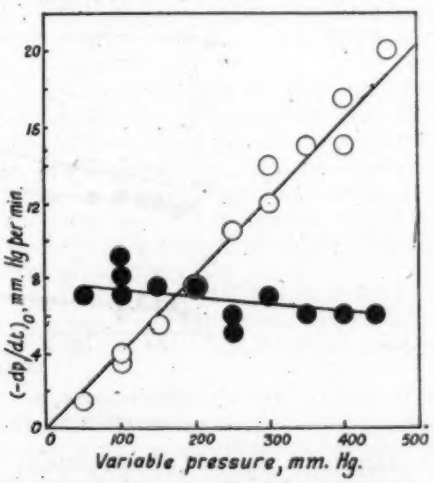
*Course of reaction in* 2 : 1 $H_2 : C_2H_2$ *mixture at* 72° *over catalyst* Ni-2.




*Initial* $H_2$ *pressure* = 399—401 *mm. Initial* $C_2H_2$ *pressure* = 199—203 *mm.*
*Significance of various types of point as in Fig.* 1.
*The two total-pressure curves shown are the extremes within which all the curves fall.*

FIG. 3.

*Effect of partial pressures on initial rate.*




*Expts.* 19—43 *on one specimen of* Ni-2. *Temperature* = 79°.
*Open circles* = 200 ± 5 *mm.* $C_2H_2$; $H_2$ *pressure varied.*
*Full circles* = 200 ± 5 *mm.* $H_2$; $C_2H_2$ *pressure varied.*

If the initial rate of ethane formation is assumed to be zero, the initial reaction can be divided into (I) $C_2H_2 + H_2 \longrightarrow C_2H_4$ and (II) $C_2H_2 + H_2 \longrightarrow$ products other than $C_2$ hydrocarbons. The results indicate that both these reactions have the same kinetics on catalysts of constant activity, being of first order with respect to hydrogen and approximately zero order with respect to acetylene.

The initial rates became less reproducible at acetylene pressures below about 50 mm., whichever gas was admitted first, but there was no sign of any great increase in rate on lowering the acetylene pressure as far as 9 mm. in the presence of 400 mm. of hydrogen at 63—83°.

Additional evidence for the kinetics described above was found in the times necessary for a pressure-fall equal to the initial hydrogen pressure, in the presence of excess of acetylene. These may be regarded as times of approximately equal fractional change, if any influence of gas pressures on the nature of the reaction is ignored. Eight experiments at 83° with 400 ± 5 mm. of acetylene and hydrogen pressures varying from 26 to 288 mm. required 32—54 minutes for pressure falls equal to the initial hydrogen pressures. The times appeared rather longer at lower hydrogen pressures, but were essentially independent of the amount of hydrogen. This is in harmony with the suggested kinetics.

The kinetic equation

$$\text{rate of fall in total pressure} = k\,[\text{hydrogen pressure}]$$

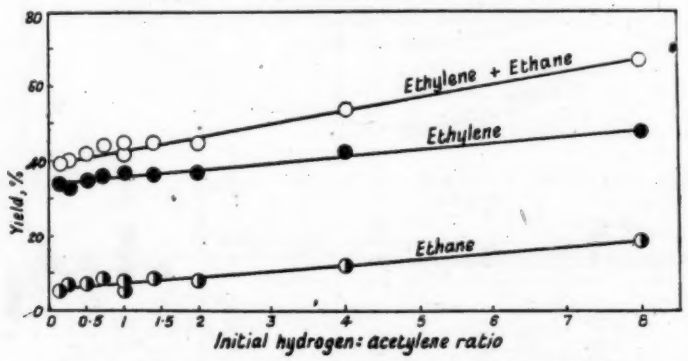
is in rough agreement with the form of the total pressure–time curves for the complete reaction up to the time when most of the acetylene is removed (Figs. 1 and 2), though it does not account for the increase in rate in the

early stages of some experiments (*e.g.*, Fig. 1) or the long period of constant rate of fall in pressure such as occurred in the experiments represented in Fig. 2. Deposition of non-volatile products on the catalyst may have some influence on the form of the pressure curves, especially in the later stages.

(vii) *The Effect of Gas Pressures on the Products from Hydrogen–Acetylene Mixtures.*—Preliminary experiments showed that the total yield of $C_2$ hydrocarbons was increased to about 60% of the acetylene not recovered with initial hydrogen : acetylene ratios of about 10. Fig. 4 shows the results of a systematic study on a catalyst of constant activity at 83°, the yields of ethylene and ethane (as percentages of the acetylene not recovered) being plotted against the initial hydrogen : acetylene ratio. For ratios below unity, the acetylene pressure was 399—401 mm. and for those above unity the hydrogen pressure was 398—400 mm. The results for 1 : 1 mixtures refer to 100 mm. and 200 mm. of each gas. Analyses were performed after a pressure fall equal to the smaller of the initial pressures. The errors were larger at the extreme ratios, but all the results agree fairly well with a linear increase in yields of both ethylene and ethane with initial hydrogen : acetylene ratio. An increase in yield of $C_2$ hydrocarbons from about 40% to 67% was caused by a 64-fold (1 : 8 to 8 : 1) increase in initial ratio. The final ratios varied from 0·05 : 1 to 16·5 : 1, a 330-fold increase. The effect of gas ratio on the $C_2$ hydrocarbon yield is therefore very slight. The rates of reaction varied by a factor of about 8, being mainly determined by the hydrogen pressure. The ratio of the ethane yield to the ethylene yield at the time of analysis rose with hydrogen : acetylene ratio, from about 1 : 7 at $H_2 : C_2H_2 = 1 : 8$ to 1 : 2·5 at $H_2 : C_2H_2 = 8 : 1$, though by no means all the acetylene had been removed even at high initial $H_2 : C_2H_2$ ratios (lowest acetylene pressure at analysis = 21 mm.).

FIG. 4.

*Effect of initial* $H_2 : C_2H_2$ *ratio on yields.*




*Experiments* 6, 8, 9, 11, 14—18, 21 *on one specimen of Ni-1.*
*Temperature* 83°.

The increase in yield of $C_2$ hydrocarbons on lowering the acetylene pressure at constant hydrogen pressure seems beyond doubt. The increase on raising the hydrogen pressure at constant acetylene pressure is perhaps scarcely outside experimental error.

These results confirm the view that the initial reactions (I) and (II) (see p. 377) have essentially the same kinetics. Reaction (I) is apparently of slightly lower order with respect to acetylene than (II), and possibly of slightly higher order with respect to hydrogen.

The ratio of the amount of hydrogen removed as products other than $C_2$ hydrocarbons to that of acetylene so removed appeared to increase with the initial hydrogen : acetylene ratio, though the error in these figures became large at ratios considerably removed from unity. Less unsaturation in the higher hydrocarbons produced, as the $H_2 : C_2H_2$ ratio is increased, is not unexpected.

The influence of gas ratio on the yields is that anticipated from the few indications of such an effect in previous work (Sabatier and Senderens, *Compt. rend.*, **1899, 128**, 1173; Ackermann, *loc. cit.*). The quantitative production of ethane from 2 : 1 hydrogen : acetylene mixtures over Raney nickel reported by Dupont (*loc. cit.*) appears to have been deduced from the fall in pressure, and no analysis of the gases is quoted. The 100% yield of ethane from 5 : 1 hydrogen : acetylene mixtures at 18 atm., reported by Petrov and Antsus (*J. Appl. Chem. U.S.S.R.*, **1933, 6**, 1145), is possibly a result of the high pressure, though on the whole unexpected. The claim (D.R.-P. 262,541) that increased yields of $C_2$ hydrocarbons can be obtained by adding one gas gradually to the other is only justified, in the case of nickel catalysts, for the addition of acetylene to hydrogen.

(viii) *Experiments with Added Ethylene.*—Over a catalyst of steady activity, the addition of 53—380 mm. of ethylene to hydrogen–acetylene mixtures caused no detectable differences in rate of fall in total pressure from the rates obtained with the same pressures of hydrogen and acetylene alone. This result is not unexpected, since during the formation of ethylene in the acetylene–hydrogen system the rate of fall in total pressure is apparently still determined mainly by the hydrogen pressure alone.

Catalysts which had been used for the hydrogen–acetylene reaction were much less active than new catalysts towards the hydrogenation of ethylene, though the induction period due to traces of oxygen (Rideal, J., 1922, **121**, 309) was not observed when catalysts previously used in the acetylene–hydrogen reaction were used to

hydrogenate ethylene. A series of experiments showed that, on the used catalysts, ethylene–hydrogen and acetylene–hydrogen mixtures of similar composition gave pressure–time curves of roughly equal slope at the same temperature, though the reproducibility was not good.

Table V shows the results of two experiments under the same conditions, except for the presence of added ethylene in one case. The significance of the headings is the same as for Tables I and II. The pressure–time curves were almost identical in shape. After deduction of the extra ethylene from the product of the second run, the figures become nearly the same for the two experiments. The acetylene–hydrogen reaction took place independently of the presence of a large ethylene pressure, although, in the absence of acetylene, the rate of ethylene hydrogenation would have been similar to that of the acetylene–hydrogen reaction.

TABLE V.

Effect of added ethylene on the products at 83° on a catalyst (Ni-1) of steady activity.

| No. of expt. | Initial pressures (mm.). | | | | | Products (mm.). | | | | | Yield, %. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$. | $C_2H_2$. | $C_2H_4$. | $\Delta p$. | $t$. | $C_2H_2$. | $C_nH_n$. | $C_2H_4$. | $H_2$. | $C_2H_6$. | $C_2H_4$. | $C_2H_6$. |
| 21 | 198 | 200 | — | 200 | 44 | 62 | 8 | 50 | 67 | 7 | 36 | 5 |
| 22 | 200 | 199 | 201 | 200 | 45 | 64 | 9 | 244 | 67 | 8 | 32 | 6 |

The results are evidence that acetylene is more strongly adsorbed on the catalyst than ethylene under similar conditions of pressure and temperature. Such an adsorption relationship is in harmony with the small production of ethane in the early stages of the hydrogen–acetylene reaction over nickel. Phenomena of this type have already been reported for platinum (Farkas and Farkas, *loc. cit.*) and palladium (Fischer and Knorr, *Z. Elektrochem.*, 1937, **43**, 608; Cremer, Knorr, and Plieninger, *loc. cit.*). Ethane formation over nickel, however, does occur to some extent even in the presence of large acetylene pressures.

(ix) *General Discussion.*—In the presence of hydrogen, hydrocarbons higher than the $C_2$ series form from acetylene over nickel at rates of the order of 100 times the rate of reaction in acetylene alone under the same conditions. The difference in speeds is so large that local overheating of the catalyst by hydrogenation reactions in the presence of hydrogen can scarcely explain it. Moreover, the effect of nickel on acetylene alone is at least to a large extent a decomposition to carbon and hydrogen. There is no evidence that such decomposition is extensive in the hydrogen–acetylene reaction under the conditions of the present experiments; but the possibility of local overheating of the catalyst playing some part in the reaction should not be entirely overlooked—*e.g.*, it is a possible cause of the early acceleration of reaction in some experiments.

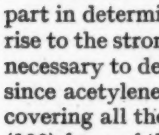
Another possible cause of this acceleration may be traces of oxygen in the gas. Addition of about 1—2 mm. of oxygen had little effect on the rate, though higher pressures of oxygen caused increasing retardation of reaction; but no induction period or accentuated acceleration effect was observed. The results of these experiments will be reported in detail later.

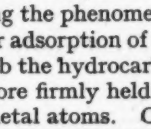
The kinetic results show that strongly adsorbed acetylene and weakly adsorbed hydrogen (or hydrogen derived directly from the gas phase) are involved in the steps which determine the rates of both the reactions (I) and (II) (see p. 377). There is little evidence of a rise in rate due to an increase in metal surface available for hydrogen as the acetylene pressure is lowered in the range studied. A negative order with respect to acetylene of this type has been reported for platinum (Farkas and Farkas, *loc. cit.*) and palladium (Cremer, Knorr, and Plieninger, *loc. cit.*). The results with nickel suggest a very strong adsorption of acetylene down to the lowest pressures investigated. Detailed discussion of the mechanism of the nickel-catalysed reaction is postponed till further experimental evidence is available.

The strong adsorption of ethylene on nickel (*e.g.*, Twigg and Rideal, *Proc. Roy. Soc.*, 1939, **171**, *A*, 55, etc.) has frequently been interpreted as a chemisorption (*e.g.*, Rideal, *Proc. Camb. Phil. Soc.*, 1939, **35**, 130; *Chem. and Ind.*, 1943, 335, etc.), and the adsorption of acetylene on nickel is thus equally probably a chemisorption phenomenon. Distances in the metal lattice have already received discussion from previous workers with regard to the theory of associative adsorption of ethylene and acetylene (Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **36**, 533; Herington, *ibid.*, 1941, **37**, 361), and it is therefore reasonable to examine what light such spatial considerations may throw on the relative strengths of adsorption of acetylene and ethylene on nickel, palladium, and platinum. Single carbon–metal bonds to these catalysts should have the following lengths, obtained by summing the single-bond radii (Pauling, " The Nature of the Chemical Bond," 1940): C–Ni, 2·0 A.; C–Pd, C–Pt each 2·1 A. The uncertainty about the valency of the metal atom could only introduce a second-order variation from these lengths. The length 1·82 A. previously used for C–Ni and C–Co in this type of calculation is the length of bonds which probably possess some double-bond character and resonance shortening (Pauling, *op. cit.*) in carbonyl-type compounds. Using the distances first mentioned, the normal lengths for C–C and C=C, and the concept of adsorption as depicted by Twigg and Rideal and by Herington, we find the most favourable lattice distances to be, in the case of ethylene, 2·87 A. for nickel and 2·94 A. for palladium and platinum, and in the case of acetylene, 3·33 A. and 3·43 A. respectively. The available distances in the face-centred cubic lattices are 2·48 A. and 3·50 A. for nickel, *ca.* 2·75 A. and 3·88 A. for palladium, *ca.* 2·75—2·85 A. and 3·88—4·04 A. for palladium hydride, and *ca.* 2·75 A. and 3·91 A. for platinum. The adsorption of ethylene on the shorter distances, which Twigg and Rideal describe in detail for nickel, should therefore also be favoured as the mode of ethylene adsorption on the other metals. When so adsorbed, the molecule would be

subject to strain, greatest in the case of nickel, which could not be relieved by a twisting of the molecule, as suggested by Twigg and Rideal, since it is readily shown that the metal–C–C angle has a maximum value when the metal–C–C–metal quadrilateral is planar. Acetylene adsorption, on this theory, would presumably favour the longer distances, as maintained by Herington with special reference to nickel and to cobalt in the face-centred cubic form. Strain would be in the opposite sense to that in the case of ethylene adsorption, and would be least with nickel catalysts. From considerations of strain alone, it seems possible that acetylene adsorption may be favoured on nickel, but in the larger lattices ethylene adsorption is likely to be more favoured. The greater abundance of shorter distances in the lattice should, if other factors were equal, favour ethylene adsorption (Herington, *loc. cit.*).

Previous workers have, of course, recognised that factors other than purely spatial ones must play a large part in determining the phenomena, and it would seem that in general it must be such other factors which give rise to the stronger adsorption of acetylene than of ethylene on the metals concerned. In particular, the energy necessary to desorb the hydrocarbon may be more important than the number of sites available for adsorption, since acetylene more firmly held than ethylene might displace the latter from the surface without necessarily covering all the metal atoms. On the associative theory such displacement appears possible on the (110) and (100) faces of the nickel–palladium–platinum group, but could hardly occur on the (111) faces, which have none of the longer lattice distances. In seeking to account for a firmer adsorption of acetylene, it may be pointed out that the heats of formation of carbon–carbon bonds are such that, in general, the addition of a substance to an acetylenic compound to give an ethylenic derivative should be accompanied by evolution of about 18 kg.-cals. more than accompanies the addition of the same substance to the ethylenic compound to give a saturated derivative. If the associative theory is correct, this energy difference may well be an important factor in accounting for the stronger adsorption of acetylenic compounds than of the corresponding ethylene derivatives, which appears rather a general phenomenon on various metals (see, *e.g.*, Campbell and Campbell, *Chem. Reviews*, 1942, **31**, 77). The difference in heats of adsorption may be increased if the unsaturated linkage concerned forms part of a conjugated resonance system, or if the greater unsaturation in the acetylene derivatives affects the adsorption in other ways, such as by permitting states of the type (I) or (II). A four-point contact of the latter type, though not probable, might be sterically possible on a (110) face.


(I.)


(II.)

It should be pointed out that the complete covering of the (110) face by associatively adsorbed acetylene (Herington, *loc. cit.*) may involve some interference between non-bonded carbon atoms, if the van der Waals radius for these is taken as about 1·5 A., which is the figure given by the approximate rule of adding 0·8 A. to the single-bond radius of the element (Pauling, *op. cit.*). In a film of adsorbed acetylene, however, there would be less interference between hydrogen atoms than in the case of ethylene, where, for total covering of the most readily covered face (110) it is necessary to take a rather low value for the van der Waals radius of hydrogen, even with the larger lattices; for instance, Twigg and Rideal (*Trans. Faraday Soc.*, 1940, **36**, 533) take 0·78 A., whereas Pauling (*op. cit.*) favours 1·2 A. as the best average figure.

It is possible that modification of the surface of the catalyst by reaction may affect adsorption relationships of the types considered.

The author is indebted to Mr. D. Ll. Hammick for help in various ways, and to the Department of Scientific and Industrial Research for a grant.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, May 10th*, 1944.]

---

# 101. *Molecular Volume and Structure. Parts VII and VIII.*

By T. W. GIBLING.

## PART VII.

Slight modification of two group values and one " interference correction " previously assessed is necessitated by recent determinations, and the parachors of aldehydes, ketones, and esters of fatty acids are reconsidered, as well as those of certain esters and ethers containing olefinic groups. Cyclic paraffins and olefins are considered in further detail. The variation of parachor with temperature in the case of certain normal liquids is discussed with special reference to the anhydrides of fatty acids.

ONLY in one instance have parachor determinations of the last few years necessitated the revision of " group values " calculated in the previous parts of this series: I and II, J., 1941, 299; III and IV, J., 1942, 661; V and VI, J., 1943, 146. Owen, Quayle, and Clegg (*J. Amer. Chem. Soc.*, 1942, **64**, 1294) measured the parachors of 15 alkyl ketones, seven of these being investigated for the first time. Their results, taken in conjunction with the earlier determinations, indicate that the values allotted in Part II for (C)·CO·(C) and (C)·CHO should each be increased by 0·1, thus becoming *51·0* and *67·4*, respectively. With these group values, calculated parachors for 41 normal liquids containing keto-groups agree with the mean observed values within 0·2% on the average. The " standard values " (S.V.) of the compounds containing the above groups (see Part III, pp. 664, 665; Part V, p. 148; Part VI, pp. 149, 150) each require the addition of 0·1 or 0·2 unit.

Sufficient data have now become available to show that the correction for the δ-carbon atom in the ethereal oxygen chain of alkyl fatty esters, as well as in the ethers themselves, is *−0·7* (Part V, p. 152). The table "Esters of Fatty Acids" (Part II, p. 307) thus requires extension and amendment as in Table I, in which are also included four esters and two ethers containing olefinic groups. For the last five compounds in this table,

TABLE I.

| Compound. | S.V., calc. | E.C. | [*P*], calc. | [*P*], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|
| Methyl *iso*butyrate * | 252·2 | +0·6 | 252·8 | 253·3 [2] | +0·2 | −2·0 : carb. β |
| *iso*Amyl formate | 293·9 | +0·8 | 294·7 | 293·65 [2] | −0·4 | −0·7 : eth. δ |
| Butyl acetate | 295·1 | +0·8 | 295·9 | 295·45 [2]†‡ | −0·1 | ,, |
| *iso*Amyl acetate | 332·7 | +1·0 | 333·7 | 334·35 [2] | +0·2 | ,, |
| Amyl acetate | 334·9 | +1·0 | 335·9 | 336·2 ‡ | +0·1 | ,, |
| *iso*Amyl propionate | 370·5 | +1·3 | 371·8 | 372·1 | +0·1 | −2·7 : carb. β; eth. δ. |
| *iso*Amyl butyrate | 409·5 | +1·6 | 411·1 | 409·7 [2] | −0·3 | −3·5 : ,, β, γ; ,, |
| *iso*Amyl stearate | 965·0 | +9·5 | 974·5 | 974·2 | −0·0 | −5·2 : ,, β, γ, δ; ,, |
| Allyl acetate | 245·0 | +0·6 | 245·6 | 245·2 § | −0·2 | — |
| αγ-Dimethylallyl formate | 282·5 | +0·7 | 283·2 | 281·6 ‖ | −0·6 | −0·7 : eth. δ |
| αγ-Dimethylallyl acetate | 321·3 | +1·0 | 322·3 | 321·2 ‖ | −0·3 | ,, |
| γ-Methyl-α-ethylallyl acetate | 361·1 | +1·3 | 362·4 | 362·3 § | −0·0 | ,, |
| αγ-Dimethylallyl methyl ether | 276·4 | +0·7 | 277·1 | 277·2 ‖ | +0·0 | ,, |
| αγ-Dimethylallyl butyl ether | 394·7 | +1·5 | 396·2 | 393·8 ‖ | −0·6 | −1·4 : 2 eth. δ |

* Inadvertently omitted from the original table (*q.v.*).
† Washburn and Shildneck (*J. Amer. Chem. Soc.*, 1933, **55**, 2354) : 294·3.
‡ Buehler, Gardner, and Clemens (*J. Org. Chem.*, 1938, **2**, 167), whose results include the following acetates: Et, 216·5; Pr, 257·0; Bu, 296·6; Am, 336·2.
§ Airs, Balfe, and Kenyon (J., 1942, 22).
‖ Hills, Kenyon, and Phillips (J., 1936, 576).

it has been assumed that the presence of a double bond in the ethereal oxygen chain does not appreciably affect the correction to be applied.

Parachors of simple *cyclo*paraffins, $C_nH_{2n}$, and *cyclo*olefins, $C_nH_{2n-2}$, have been determined for $n = 5$—7, as well as parachors of several of their derivatives, and in Part III (*loc. cit.*) those of *cyclo*pentane and *cyclo*hexane and some of their derivatives were considered. So far, no values have been recorded for the parachors of the parent hydrocarbons in which $n = 3$ or 4, or for those of any of their homologues, but certain derivatives have been investigated. Table II gives probable values for (*a*) ring corrections, (*b*) S.V., and (*c*) parachor of the parent hydrocarbon in each case, but data are lacking for *cyclo*propene and *cyclo*butene rings. Parachors asterisked in this table were determined by Vogel (J., 1938, 1323).

TABLE II.

| | *cyclo*Paraffins, $C_nH_{2n}$. | | | *cyclo*Olefins, $C_nH_{2n-2}$. | | |
|---|---|---|---|---|---|---|
| *n*. | (*a*). | (*b*). | (*c*). | (*a*). | (*b*). | (*c*). |
| 3 | + 5·9 | 131·9 | 132·0 | — | — | — |
| 4 | + 0·1 | 168·1 | 168·3 | — | — | — |
| 5 | − 5·4 | 204·6 | 205·0 * | − 6·5 | 192·5 | 192·8 * |
| 6 | −10·7 | 241·3 | 241·8 * | −11·1 | 229·9 | 230·4 * |
| 7 | −15·9 | 278·1 | 278·8 * | −15·5 | 267·5 | 268·2 * |

The above values of (*a*), (*b*), and (*c*) for *cyclo*paraffins lie smoothly on their respective curves, and the ring corrections (*a*) are determinable from the general formula $26·1—7·63n + 0·35n^2 - 0·016n^3$. The values for *cyclo*butane were obtained by interpolation, their approximate accuracy being indicated by good agreement of three of the four derivatives included in Table III, the calculated and observed parachors in which are supplementary to those given in Part III (*loc. cit.*, p. 662). The compounds in question are (A) methyl and (B) ethyl *cyclo*propane-1 : 1-dicarboxylate, (C) ethyl *cyclo*propane-1 : 2-dicarboxylate, (D) ethyl caronate, (E) *cyclo*-

TABLE III.

Derivatives of *cyclo*paraffins, $C_nH_{2n}$.

| *n*. | Cpd. | S.V., calc. | E.C. | [*P*], calc. | [*P*], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|---|
| 3 | (A) | 337·9 | +1·1 | 339·0 | 339·3 | +0·1 | −2·2 : // chains |
| ,, | (B) | 414·5 | +1·7 | 416·2 | 417·1 | +0·2 | −4·4 : ,, |
| ,, | (C) | 421·1 | +1·7 | 422·8 | 422·8 | ±0·0 | — |
| ,, | (D) | 491·1 | +2·4 | 493·5 | 493·2 | −0·1 | −5·4 : 2*o*- |
| ,, | (E) | 697·1 | +4·9 | 702·0 | 701·1 | −0·1 | −14·2 : 2*o*-; // chains |
| 4 | (F) | 312·7 | +0·9 | 313·6 | 309·4 | −1·3 | — |
| ,, | (G) | 374·1 | +1·4 | 375·5 | 374·8 | −0·2 | −2·2 : // chains |
| ,, | (H) | 450·7 | +2·0 | 452·7 | 454·1 | +0·3 | −4·4; ,, |
| ,, | (I) | 360·7 | +1·3 | 362·0 | 362·0 * | ±0·0 | — |
| | | | | *cyclo*Olefins, $C_nH_{2n-2}$. | | | |
| 5 | (J) | 231·3 | +0·5 | 231·8 | 232·9 | +0·5 | — |
| 6 | (K) | 268·7 | +0·7 | 269·4 | 269·4 | ±0·0 | — |

* [*P*] increased from 358·1 at 13·5°, fairly rapidly at first (to 359·5 at 46°), later more slowly (361·1 at 84·5°, 361·5 at 111·5°) till it had reached 361·7 at 126·5°; extrapolation indicates the calc. value, 362·0.

propane-1 : 1 : 2 : 2-tetracarboxylate, (F) ethyl *cyclo*butanecarboxylate, (G) methyl and (H) ethyl *cyclo*butane-1 : 1-dicarboxylate, (I) ethyl 1-cyano*cyclo*butane-1-carboxylate, (J) 1-methyl-$\Delta^2$-*cyclo*pentene, (K) 1-methyl-$\Delta^1$-*cyclo*hexene. A correction of $-3{\cdot}2$ is made for attachment of a carbon atom to the ring; other corrections applied here or later include *o*-, *m*-, and *p*-corrections (as for the xylenes) and those for parallel chains of carbon atoms (as for alkyl malonates; see Part II, p. 309). Parachors recorded in Table III are by Sugden and Walters (J., 1927, 139), except those of (A), (G), (J), and (K), which are by Vogel (J., 1934, 333; 1938, 1323).

The following table is supplementary to that in Part III (p. 664) in which, as stated before, 0·1 should be added to each S.V.

| Cyclic ketone. | S.V., calc. | E.C. | [*P*], calc. | [*P*], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|
| 1-Methyl-$\Delta^1$-*cyclo*hexen-3-one ..... | 277·2 | +0·7 | 277·9 | 279·0 * | +0·4 | −1·7 : *m*- |
| *l*-Menthone ..... | 400·8 | +1·6 | 402·4 | 402·15 [2] † | −0·1 | −6·6 : *o*-, *m*-, *p*- |
| *dl-iso*Menthone ..... | 400·8 | +1·6 | 402·4 | 403·25 [2] † | +0·2 | ,, |
| *dl*-Angustione ..... | 440·8 | +1·9 | 442·7 | 442 ‡ | −0·2 | −24·7 : 4*o*-, 3*m*-, 4*p*- |

* Naves and Papazian (*Helv. Chim. Acta*, 1942, **25**, 1046).

† Carter (J., 1927, 1278) : *l*-, 403·2; *dl-iso*-, 405·3. Gillespie, Macbeth, and Mills (J., 1940, 280) : *l*-, 401·1; *dl-iso*-, 401·2.

‡ Evans and Soper (J., 1931, 289).

It may be noted that the parachor calculated for angustione (I), with its multiple *o*-, *m*-, and *p*-corrections, agrees well with the experimental value.

From the parachor of ethylene oxide, 112·5 (Sugden and Wilkins, J., 1927, 139), the ring correction in this appears to be $-1{\cdot}7$. Thus :

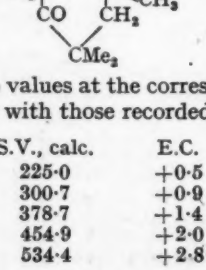
| | | | |
|---|---|---|---|
| 2-$CH_2$-, uncorr. at 42·0 (Part I, p. 302)..... | 84·0 | S.V. ..... | 112·4 |
| -O-, ,, 26·7 (Part VI, p. 150) ..... | 26·7 | E.C. ..... | +0·1 |
| Σ group values ..... | 110·7 | [*P*] ..... | 112·5 |
| Ring correction ..... | +1·7 | | |

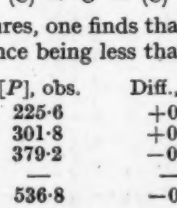
The fact that the parachor of water is greater the more fully its molecules are associated, in contrast to alcohols and phenols, whose parachors decrease with association (Part VI, p. 150), confirms the idea that $H_2O$ molecules tend to associate in *small* rings, for which the increase in volume due to the presence of the ring itself is not swamped by a decrease brought about by interaction of the non-linked atoms of the ring (Part III, p. 661); an alcohol or a phenol, with carbon as well as hydrogen attached to the oxygen atom, tends to form open chains of molecules.

The earliest determinations of parachors showed clearly that those of non-associated substances, such as carbon tetrachloride, ether, ethyl acetate, and nitrobenzene, remained constant over wide temperature ranges. In certain cases, however, parachors of non-associated liquids have been found to vary considerably with temperature, the substances in question usually having molecules which are both polar and flexible.

Lewis's results (J., 1940, 32) show that the parachors of the anhydrides of four of the fatty acids all increase by just over a unit for a rise in temperature of 30° within the range of determination, *viz.*, 15° or 20° to 50°. He remarks that the presence of small traces of the associated acids would contribute to the anomaly, but Sugden's results (J., 1924, **125**, 37; " The Parachor and Valency," 1929, 167) for the parachor of acetic acid at different temperatures suggest that contamination of acetic anhydride with its acid should act in the reverse direction, *i.e.*, tend to reduce the anomaly. Thus, the parachor of acetic acid, treated as being in the dimeric state, increases from 262·6 at 10° to 263·4 at 50°, *i.e.*, only by 0·8, or 0·3%, for a temperature rise of 40°, whereas that of Lewis's acetic anhydride increases from 225·4 at 15° to 226·6 at 50°, *i.e.*, by 1·2, or 0·5%, for a rise of 35°. The parachor values of this series of anhydrides are consistent with each other at any one of the seven or eight temperatures used, and therefore the anomaly would appear to be connected with the structure of the –CO·O·CO·– grouping, the effective value of which seems to vary as follows :

| Temp. ..... | 15° | 20° | 25° | 30° | 35° | 40° | 45° | 50° |
|---|---|---|---|---|---|---|---|---|
| S.V. ..... | 114·5 | 114·6 | 114·7 | 114·9 | 115·1 | 115·3 | 115·5 | 115·7 |

(I.) 

(II.)

Using the above group values at the corresponding temperatures, one finds that the 30 parachors calculated show excellent agreement with those recorded, the mean difference being less than 0·1%. Thus, at 20° :

| Anhydride. | S.V., calc. | E.C. | [*P*], calc. | [*P*], obs. | Diff., %. | Diff. in S.V. for 2-$CH_2$-.* |
|---|---|---|---|---|---|---|
| Acetic ..... | 225·0 | +0·5 | 225·5 | 225·6 | +0·0 | — |
| Propionic ..... | 300·7 | +0·9 | 301·6 | 301·8 | +0·1 | 2 × 37·8 |
| Butyric ..... | 378·7 | +1·4 | 380·1 | 379·2 | −0·2 | 2 × 39·0 |
| Valeric ..... | 454·9 | +2·0 | 456·9 | — | — | 2 × 38·1 |
| Hexoic ..... | 534·4 | +2·8 | 537·2 | 536·8 | −0·1 | 2 × 39·8 |

* See Part II, p. 306.

From consideration of the structure of the anhydride group, it is clear that its effective volume contribution will depend upon the relative positions in space of the two carbonyl groups attached to the ethereal oxygen atom, the different possible configurations being obtained by rotation of the attached groups round either of the axes (1) and (2) in (II). Configurations producing least interference (and therefore leading to greatest molecular volume) should be those in which the planes of the two halves of the anhydride group are approximately at right angles to each other (cf. the somewhat similar case of benzil; Part III, p. 665). The more nearly the structure of the group becomes planar, the greater will be the interference, and consequently the smaller the parachor contribution.

In some cases, notably with the *tert.*-alkyl chlorides investigated by Quayle, Owen, and Beavers (*J. Amer. Chem. Soc.*, **1939**, **61**, 3107), parachors of normal liquids have been found to *decrease* with rise in temperature, and in a few cases parachors seem to increase to a maximum value and then decrease with further rise in temperature (Part V, p. 147). Where parachors show a decided drift in one direction or the other, a mean value recorded over some arbitrary range of temperature can obviously have little significance.

## Part VIII.

The parachors of alkyl sulphides, thiols, and disulphides are considered, and group values are estimated. It is suggested that the "interference corrections", varying from member to member, which are required for the parachors of mercury alkylmercaptides, afford evidence as to the structure of these compounds. The structures of alkyl sulphites are similar to those of the corresponding alkyl carbonates, and those of sulphates and phosphates also appear to belong to the same type as the sulphites.

From the most recent determinations of the parachors of alkyl sulphides, thiols, and disulphides, standard values for groups have been estimated as follows: (C)·S·(C), *52·0*; (C)·SH, *68·2*; (C)·S·S·(C), *103·1*; (C)·$CH_2$·(S), *39·3*, whence the correction for the grouping (III) is *−2·7*. These values have been obtained by fixing S.V., $-CH_3$ at 55·2 (see Part II, p. 304). In all three classes of compound the alkyl chain would appear to bend backwards towards the sulphur atom to which it is attached. The "interference corrections" required extend as far as the fifth carbon atom, those for the disulphides necessarily including a correction for the β-carbon atom, due to interaction between this and the second sulphur atom.

(III.)

The $CH_2$ increments in the series are as follows:

| | Et. | Pr. | Bu. | Am. | Hex. |
|---|---|---|---|---|---|
| Sulphides and thiols ..... | 39·3 | 38·8 | 39·2 | 38·8 | 39·8, normally |
| Disulphides..... | 38·4 | 38·5 | 39·2 | 38·8 | —. |

Hence, if normal values are given to the alkyl groups [*viz.*, $CH_3$·(C), 55·2; (C)·$CH_2$·(C), 39·8; (C)·$CH_2$(S), 39·3; $\begin{matrix}(C)\\(C)\end{matrix}\!\!>$CH·(C), 22·2], the corrections required in the chain are as follows, these applying to only one of the branches in a divided chain:

| ——S——$\overset{\alpha}{CH_2}$——$\overset{\beta}{CH_2}$——$\overset{\gamma}{CH_2}$——$\overset{\delta}{CH_2}$——$\overset{\epsilon}{CH_2}$—— | | | | | |
|---|---|---|---|---|---|
| Sulphides and thiols ..... | | | −1·0 | −0·6 | −1·0; total, −2·6 |
| Disulphides ..... | | −0·9 | −1·3 | −0·6 | −1·0; ,, −3·8 |

In the following table the results for *iso*propyl and *sec.*- and *tert.*-butyl compounds are omitted, since the exact configurations of the molecules, and consequently the corrections required, are not obvious. The parachors of the sulphides and disulphides were measured by Vogel and Cowan (J., **1943**, 16) and those of the thiols by Mann and Purdie (J., **1935**, 1557), except ethylthiol and phenylthiol, whose parachors were recorded by Sugden, Reed, and Wilkins (J., **1925**, **127**, 1525). In the calculations for phenyl compounds it is assumed that interference between the sulphur atom and the benzene ring necessitates a correction of *−2·7*, *i.e.*, that S.V., $C_6H_5$·(S) is *189·7* (cf. Part III, p. 664 for oxygen attached to the ring).

*Sulphides*, R·S·R′.

| R and R′. | S.V., calc. | E.C. | [*P*], calc. | [*P*], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|
| Dimethyl ..... | 162·4 | +0·2 | 162·6 | 163·1 | +0·3 | — |
| Methyl ethyl ..... | 201·7 | +0·4 | 202·1 | 201·9 | −0·1 | — |
| Diethyl ..... | 241·0 | +0·5 | 241·5 | 241·5 | ±0·0 | — |
| Methyl *iso*butyl ..... | 278·1 | +0·7 | 278·8 | 279·6 | +0·3 | −1·0: S$\gamma$ |
| Methyl butyl ..... | 279·7 | +0·7 | 280·4 | 280·1 | −0·1 | −1·6: S$\gamma$, $\delta$ |
| Dipropyl ..... | 318·6 | +1·0 | 319·6 | 318·9 | −0·2 | −2·0: S 2$\gamma$ |
| Ethyl butyl ..... | 319·0 | +1·0 | 320·0 | 320·3 | +0·1 | −1·6: S $\gamma$, $\delta$ |
| Di*iso*butyl ..... | 393·8 | +1·5 | 395·3 | 395·4 | +0·0 | −2·0: S 2$\gamma$ |
| Dibutyl ..... | 397·0 | +1·5 | 398·5 | 399·3 | +0·2 | −3·2: S 2$\gamma$, 2$\delta$ |
| Di*iso*amyl ..... | 472·2 | +2·2 | 474·4 | 472·9 | −0·3 | ,, |
| Diamyl ..... | 474·6 | +2·2 | 476·8 | 477·0 | +0·0 | −5·2: S 2$\gamma$, 2$\delta$, 2$\epsilon$ |
| Dihexyl ..... | 554·2 | +3·0 | 557·2 | 556·5 | −0·1 | ,, |
| Diheptyl ..... | 633·8 | +4·0 | 637·8 | 638·4 | +0·1 | ,, |
| Dioctyl ..... | 713·4 | +5·2 | 718·6 | 718·0 | −0·1 | ,, |
| Diphenyl..... | 426·6 | +1·8 | 428·4 | 428·0 | −0·1 | −4·8: as 2EtPh |

*Thiols*, R·SH.

| R and R'. | S.V., calc. | E.C. | [*P*], calc. | ]*P*], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|
| Ethyl | 162·7 | +0·2 | 162·9 | 162·9 | ±0·0 | — |
| Amyl | 279·5 | +0·7 | 280·2 | 280·6 | +0·1 | −2·6 : S $\gamma$, $\delta$, $\epsilon$ |
| Heptyl | 359·1 | +1·2 | 360·3 | 360·3 | ±0·0 | ,, |
| Octyl | 398·9 | +1·5 | 400·4 | 400·2 | −0·0 | ,, |
| Phenyl | 257·9 | +0·6 | 258·5 | 257·0 | −0·6 | — |

*Disulphides*, $R_2S_2$.

| | | | | | | |
|---|---|---|---|---|---|---|
| Methyl | 213·5 | +0·4 | 213·9 | 213·9 | ±0·0 | — |
| Ethyl | 290·3 | +0·8 | 291·1 | 291·1 | ±0·0 | −1·8 : $S_2$ 2$\beta$ |
| Propyl | 367·3 | +1·3 | 368·6 | 368·5 | −0·0 | −4·4 : $S_2$ 2$\beta$, 2$\gamma$ |
| *iso*Butyl | 441·5 | +1·9 | 443·4 | 443·4 | ±0·0 | ,, |
| Butyl | 445·7 | +1·9 | 447·6 | 447·7 | +0·0 | −5·6 : $S_2$ 2$\beta$, 2$\gamma$, 2$\delta$ |
| *iso*Amyl | 520·9 | +2·7 | 523·6 | 521·2 * | −0·5 | ,, |
| Amyl | 523·3 | +2·7 | 526·0 | 524·6 * | −0·3 | −7·6 : $S_2$ 2$\beta$, 2$\gamma$, 2$\delta$, 2$\epsilon$ |

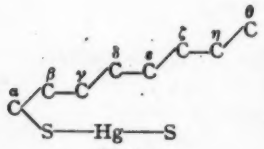
* These parachors increase rather rapidly with rise in temperature: 518·5 (13·4°) to 522·9 (120·2°) and 522·0 (18·5°) to 525·6 (120·7°), respectively.

The interference corrections required by the parachors of mercury *n*-alkylmercaptides suggest, in the liquid state, zig-zag configurations of the alkyl chains on opposite sides of the S–Hg–S nucleus, itself known to have a linear structure (IV) [cf., however, Wells (*Z. Krist.*, 1937, *A*, **96**, 435) on the crystal structures]. Mann and Purdie (*loc. cit.*, p. 1562) recorded the parachors of six members of the series at two temperatures and that of the butyl compound at the higher temperature, 99°, only. Their results show an average increase in parachor of 2·9 per 22° rise in temperature. For purposes of comparison throughout the series, therefore, it is best to consider only the values measured at 99°. In the following table, "S.V., expd." is obtained by addition to the value for the ethyl compound of $2(n - 2) \times 39{\cdot}8$, where $n$ is the number of carbon atoms in each alkyl chain. As might be expected from the configuration suggested, the corrections form two descending series—one for the odd-numbered carbon atoms (−6·1, −4·35, −3·55) and one for the even (−4·3, −3·0, −1·1)—and appear to diminish practically to zero when the eighth carbon atom is reached.

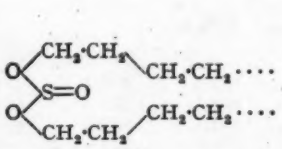
*Mercury alkylmercaptides*, $Hg(SR)_2$.

| R. | [*P*], obs. | E.C. | S.V., obs. | S.V., expd. | Corrn. | Corrn. per C atom. |
|---|---|---|---|---|---|---|
| Ethyl | 335·5 | −1·1 | 334·4 | (334·4) | — | — |
| Propyl | 403·4 | −1·6 | 401·8 | 414·0 | −12·2 | $\gamma$, −6·1 |
| Butyl | 475·0 | −2·2 | 472·8 | 493·6 | −20·8 | $\delta$, −4·3 |
| Amyl | 546·6 | −2·9 | 543·7 | 573·2 | −29·5 | $\epsilon$, −4·35 |
| Hexyl | 621·1 | −3·8 | 617·3 | 652·8 | −35·5 | $\zeta$, −3·0 |
| Heptyl | 694·5 | −4·7 | 689·8 | 732·4 | −42·6 | $\eta$, −3·55 |
| Octyl | 773·1 | −5·9 | 767·2 | 812·0 | −44·8 | $\theta$, −1·1 |

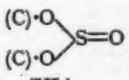
The structure of alkyl sulphites (V) resembles that of the carbonates (Part II, p. 308), and the parachor corrections are identical, except that the β-carbon atom in each chain, by its interaction with the sulphite group (which is larger than the carbonate group), produces an interference for which the correction is *−0·8*. In the case of *iso*propyl sulphite, however, the correction is not operative, which suggests that each pair of methyl groups in this molecule is symmetrically arranged with respect to the plane of the $SO_3$ nucleus. In alkyl sulphates and phosphates, also, the alkyl chains beyond the β-carbon atoms seem to proceed parallel with each other, each pair of corresponding carbon atoms being at such a distance apart as to cause mutual inter-



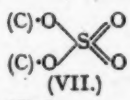
(IV.)



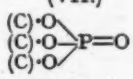
(V.)



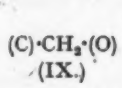
(VI.)



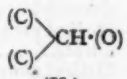
(VII.)



(VIII.)



(IX.)



(X.)

ference necessitating a correction of *−2·2*. As the phosphates contain three alkyl chains, the correction for the interaction of each trio of corresponding carbon atoms beyond β will be *−6·6*. In both cases there is a correction for interference between the β-atom and the $SO_4$ or $PO_4$ group: for the former, *−1·1*, and for the latter, *−1·4*. The following are the S.V. of the sulphite, sulphate, and phosphate groups, respectively: (VI), *109·0*; (VII), *127·0*; (VIII), *119·8*. [N.B. S.V., (IX) = 39·4; S.V., (X) = 21·4—see Part II, p. 305]. All the parachor measurements are by Vogel and Cowan (*loc. cit.*, p. 22), who also give details of previous determinations in some cases.

*Alkyl sulphites*, $R_2SO_3$.

| R. | S.V., calc. | E.C. | [P], calc. | [P], obs. | Diff., %. | Corrns. applied. |
|---|---|---|---|---|---|---|
| Methyl | 219·4 | +0·4 | 219·8 | 219·7 | −0·0 | — |
| Ethyl | 296·6 | +0·8 | 297·4 | 297·6 | +0·1 | −1·6 : $SO_3$ 2$\beta$ |
| *iso*Propyl | 372·8 | +1·3 | 374·1 | 374·5 | +0·1 | — |
| Propyl | 374·0 | +1·4 | 375·4 | 375·4 | ±0·0 | −3·8 : $SO_3$ 2$\beta$; // chns. |
| *iso*Butyl | 447·0 | +2·0 | 449·0 | 450·6 | +0·4 | −6·0 : „ „ |
| Butyl | 451·4 | +2·0 | 453·4 | 452·5 | −0·2 | „ „ „ |
| *iso*Amyl | 524·4 | +2·7 | 527·1 | 525·7 | −0·3 | −8·2 : „ „ |
| Amyl | 528·8 | +2·8 | 531·6 | 532·0 | +0·1 | „ „ „ |

*Alkyl sulphates*, $R_2SO_4$.

| | | | | | | |
|---|---|---|---|---|---|---|
| Methyl | 237·4 | +0·5 | 237·9 | 237·9 | ±0·0 | — |
| Ethyl | 314·0 | +0·9 | 314·9 | 316·4 | +0·5 | −2·2 : $SO_4$ 2$\beta$ |
| Propyl | 391·4 | +1·5 | 392·9 | 392·2 | −0·2 | −4·4 : „ ; // chns. |
| Butyl | 468·8 | +2·1 | 470·9 | 469·9 | −0·2 | −6·6 : „ „ |

*Alkyl phosphates*, $R_3PO_4$.

| | | | | | | |
|---|---|---|---|---|---|---|
| Methyl | 285·4 | +0·8 | 286·2 | 286·2 | ±0·0 | — |
| Ethyl | 399·5 | +1·5 | 401·0 | 399·9 | −0·3 | − 4·2 : $PO_4$ 3$\beta$ |
| Propyl | 512·2 | +2·6 | 514·8 | 515·9 | +0·2 | −10·8 : „ ; // chns. |
| Butyl | 625·0 | +3·9 | 628·9 | 629·2 | −0·0 | −17·4 : „ „ |

The three pairs of methyl groups at the end of the molecule of an *iso*-alkyl phosphate will presumably take up a symmetrical structure about the axis of the $PO_4$ group, but the interference corrections involved are not calculable from present data; from the parachors determined for *iso*propyl phosphate (509·9) and *iso*butyl phosphate (625·2), the corrections required (−8·9 and −14·5, respectively) seem to be intermediate between those calculated for the normal isomer and the preceding normal homologue in each case.

New or amended group values recorded in these two parts are as follows: S.V., (C)·CO·(C), 51·0; (C)·CHO, 67·4; (C)·CO·O·CO·(C), varying from 114·5 at 15° to 115·7 at 50°; (C)·S·(C), 52·0; (C)·SH, 68·2; (C)·S·S·(C), 103·1; (C)·$CH_2$·(S), 39·3; $C_6H_5$·(S), 189·7; [(C)·O]$_2$SO, 109·0; [(C)·O]$_2SO_2$, 127·0; [(C)·O]$_3$PO, 119·8.

Correction for the grouping $C\begin{cases}C\\S\end{cases}$, −2·7.

Corrections for carbon atoms in alkyl chains attached to:

–O–: δ, −0·7. –S–: γ, −1·0; δ, −0·6; ε, −1·0 (total, −2·6).
–S·S–: β, −0·9; γ, −1·3; δ, −0·6; ε, −1·0 (total, −3·8).
–O·SO·O–: β, −0·8 (−2·2 extra for each following pair of C atoms).
–O·$SO_2$·O–: β, −1·1(−2·2 extra for each following pair of C atoms).
$\left.\begin{matrix}-O\\-O\end{matrix}\right\rangle$PO·O–: β, −1·4 (−6·6 extra for each following trio of C atoms).

Ring corrections: Derivatives of *cyclo*paraffins, $C_nH_{2n}$, with $n = 3$, +5·9; 4, +0·1; 5, −5·4; 6, −10·7; 7, −15·9; *i.e.*, $26·1—7·63n + 0·35n^2 - 0·016n^3$. Derivatives of *cyclo*olefins, $C_nH_{2n-2}$, with $n = 5$, −6·5; 6, −11·1; 7, −15·5.

THE GRAMMAR SCHOOL OF QUEEN ELIZABETH, WAKEFIELD. [*Received, May 26th*, 1944.]

## 102. *The Separation of 3-Nitro-1-naphthylamine and 4-Nitro-2-naphthylamine by Maleic Anhydride, and the Monobromination of 4-Nitro-2-naphthylamine.*

By HERBERT H. HODGSON and DAVID E. HATHWAY.

A mixture of 4-nitro-2-naphthylamine and 3-nitro-1-naphthylamine has been separated by preferential acylation of the former compound by maleic anhydride. A thermal analysis diagram has been constructed to enable both the acetic anhydride and the maleic anhydride separation to be almost quantitatively effected. Two equivalents or more of bromine will only monobrominate 4-nitro-2-naphthylamine to give 1-bromo-4-nitro-2-naphthylamine. Reduction of 1 : 3-dinitronaphthalene by sodium hyposulphite gives 1 : 3-naphthylenediamine.

THE separation of 4-nitro-2-naphthylamine from 3-nitro-1-naphthylamine, previously effected with acetic anhydride (Hodgson and Birtwell, this vol., p. 75), has now been accomplished with maleic anhydride. A thermal analysis diagram has been constructed to enable the requisite amount of acetic or maleic anhydride to be computed.

The mixed amines obtained by sodium sulphide reduction of 1 : 3-dinitronaphthalene (Hodgson and Birtwell, *loc. cit.*) comprise *ca.* 16% of 4-nitro-2- and 84% of 3-nitro-1-naphthylamine, as deduced from the m. p. 114° of the mixture and subsequent isolation of the separate amines. Reduction in glacial acetic acid by

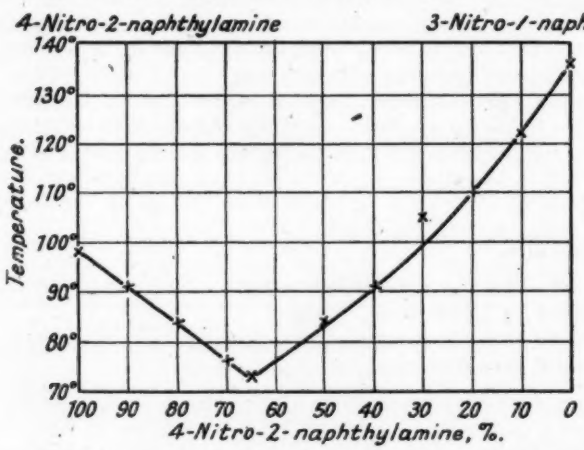
alcoholic stannous chloride (Vesely and Dvorăk, *Bull. Soc. chim.*, 1923, **33**, 319) gave a mixture of amines, m. p. 120°, corresponding to 11% of 4-nitro-2- and 89% of 3-nitro-1-naphthylamine. Reduction of 1 : 3-dinitronaphthalene with sodium hyposulphite (hydros) in amount just sufficient for monoreduction gave equal quantities of 1 : 3-naphthylenediamine and unchanged 1 : 3-dinitronaphthalene; no nitronaphthylamines were detected.

Bromination of 4-nitro-2-naphthylamine differs from that of its isomeride in that more than 2 equivalents of bromine will only effect monobromination to 1-bromo-4-nitro-2-naphthylamine, whereas less than one equivalent of bromine will dibrominate 3-nitro-1-naphthylamine to 2 : 4-dibromo-3-nitro-1-naphthylamine, leaving unchanged initial material (Hodgson and Hathway, this vol., p. 21). The constitution of the 1-bromo-4-nitro-2-naphthylamine was confirmed by its deamination to 1-bromo-4-nitronaphthalene.

## Experimental.

*Separation of* 4-*Nitro*-2- *from* 3-*Nitro*-1-*naphthylamine.*—When hot solutions of maleic anhydride (0·5 g.) and the mixed amines (4 g.) obtained by sodium sulphide reduction of 1 : 3-dinitronaphthalene (Hodgson and Birtwell, *loc. cit.*) in chloroform (5 c.c. and 30 c.c. respectively) were mixed, heat was evolved, and *4-nitro-2-naphthylmaleamic acid* separated on cooling (1·35 g.); it crystallised from ethyl alcohol in pale lemon, parallelepipeds, m. p. 193° (Found : N, 9·7. $C_{14}H_{10}O_5N_2$ requires N, 9·8%). Three successive additions of maleic anhydride (0·2 g.) to the filtrate effected further separations (0·55 g.) of the above compound, contaminated, however, by an increasing content of 3-nitro-1-naphthylmaleamic acid as shown by m. p. sequences of 178°, 171, and 165°. Further addition of maleic anhydride afforded pure *3-nitro-1-naphthylmaleamic acid*, which crystallised from alcohol (charcoal) in sheaves of slender golden-yellow needles, m. p. 170° (Found : N, 9·7%). Mixed m. p.'s with the maleamic acids prepared from the pure nitroamines established identity. Both the above maleamic acids dissolve in aqueous sodium carbonate and are precipitated unchanged from the solutions on acidification.

4-Nitro-2-naphthylamine was isolated from the maleamic acid (1·3 g.) by heating it for 1 hour under reflux with a mixture of sulphuric acid (15 c.c., *d* 1·84), ethyl alcohol (30 c.c.), and water (15 c.c.), precipitation of 4-nitro-2-naphthylamine sulphate by addition of water (150 c.c.), and subsequent basification by cautious addition of 10% aqueous ammonia at 0°; it crystallised from 50% aqueous ethyl alcohol in long, felted, scarlet needles, m. p. 98·5° (Veselý and Dvorăk, *loc. cit.*, give m. p. 95°; Hodgson and Birtwell, *loc. cit.*, give m. p. 97°) (Found : N, 14·9. Calc. : N, 14·9%). It gave an apple-green colour with concentrated sulphuric acid which became scarlet on dilution, whereas 3-nitro-1-naphthylamine gave an intense dirty brown colour with a green fluorescence, also turning scarlet on dilution.




*4-Nitrobenzo-2-naphthalide*, prepared by the Schotten–Baumann reaction in acetone, crystallised from ethyl alcohol in golden-yellow plates, m. p. 169° (Found : N, 9·6. $C_{17}H_{12}O_3N_2$ requires N, 9·6%).

*Thermal Analysis of Mixtures of* 3-*Nitro*-1- *and* 4-*Nitro*-2-*naphthylamine.*—Synthetic mixtures of the pure nitroamines were fused in ignition tubes, the melt allowed to solidify, then finely powdered, and the m. p. taken when the sintered substance just became a clear liquid. The results are plotted in the diagram. The eutectic temperature is 73° and a synthetic mixture having the eutectic composition, *viz.*, 35% of 3-nitro-1-naphthylamine (0·035 g.) and 65% of 4-nitro-2-naphthylamine (0·065 g.), was found to melt at 73°.

The mixed amines (7·4 g.) obtained by reduction of 1 : 3-dinitronaphthalene (11 g.) by sodium sulphide (Hodgson and Birtwell, *loc. cit.*) had m. p. 114°, corresponding to 16% of 4-nitro-2- and 84% of 3-nitro-1-naphthylamine; separation by maleic anhydride resulted in the isolation of pure 4-nitro-2-naphthylamine (0·8 g., *ca.* 70% of the predicted yield) and of 3-nitro-1-naphthylamine (6·5 g., m. p. 129°, of 95% purity).

*Monobromination of* 4-*Nitro*-2-*naphthylamine.*—When 4-nitro-2-naphthylamine (2 g.), dissolved in dry chloroform (9 c.c.), was treated dropwise at 40—50° with 4·7 c.c. of a solution of bromine (1 c.c.) in dry chloroform (9 c.c.), 1-bromo-4-nitro-2-naphthylamine hydrobromide (3·2 g.) was precipitated. Dilute aqueous ammonia liberated *1-bromo-4-nitro-2-naphthylamine* (2·8 g.), which crystallised from alcohol (charcoal) in felted tan-coloured parallelepipeds, m. p. 153° (Found : Br, 29·8. $C_{10}H_7O_2N_2Br$ requires Br, 30·0%). *1-Bromo-4-nitroaceto-2-naphthalide* crystallised from glacial acetic acid in buff, almost colourless, rectangular plates, m. p. 177° (Found : Br, 25·7. $C_{12}H_9O_3N_2Br$ requires Br, 25·9%).

1-Bromo-4-nitronaphthalene was formed when a solution of 1-bromo-4-nitro-2-naphthylamine (1·3 g.) in glacial acetic acid (30 c.c.) was stirred below 20° into one of sodium nitrite (0·5 g.) in sulphuric acid (7 c.c., *d* 1·84) and the diazonium mixture, after 15 minutes, stirred into a suspension of cuprous oxide (1 g.) in ethyl alcohol (50 c.c.), the stirring being continued until reaction ceased. The mixture was poured into ice-water (500 c.c.), and 1-bromo-4-nitronaphthalene extracted from the resulting precipitate by boiling alcohol (1 g.), from which it crystallised on cooling: recrystallised (charcoal) from the same solvent, it formed pale yellow micro-needles, m. p. 87° (John, *Bull. Soc. chim.*, 1877, **28**, 515, gives m. p. 85°) (Found : Br, 31·5. Calc. : Br, 31·7%).

*Attempted Dibromination of* 4-*Nitro*-2-*naphthylamine.*—A solution of the amine (0·3 g.) in dry chloroform (2 c.c.) at 50° was treated with 2 c.c. of the bromine reagent above, and the precipitated hydrobromide removed and basified. Only 1-bromo-4-nitro-2-naphthylamine (0·35 g.) was obtained, which, after recrystallisation from alcohol, had m. p. and mixed m. p. with authentic specimen, 153°. *4-Nitronaphthalene-2-azo-β-naphthol* was precipitated when a solution of 4-nitro-2-naphthylamine (0·5 g.) in glacial acetic acid (7 c.c.) was diazotised by addition to sodium nitrite (0·3 g.) in sulphuric acid (5 c.c., *d* 1·84) below 20°; after 30 minutes, the solution was diluted with ice and stirred into one of β-naphthol (0·4 g.) in 20% aqueous sodium hydroxide (55 c.c.) below 25°. After 1 hour, the azo-compound (0·9 g.) was removed and crystallised from glacial acetic acid; it formed deep red, micro-needles, m. p. 240° (Found : N, 12·3.

$C_{20}H_{13}O_2N_3$ requires N, 12·2%), which gave with concentrated sulphuric acid a deep purple colour that turned scarlet on dilution with water.

The authors thank I.C.I. Ltd., Dyestuffs Division, for gifts of chemicals.

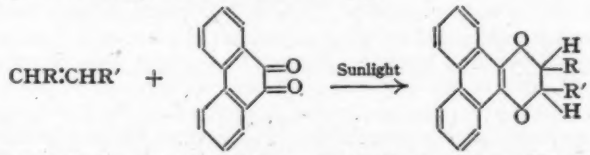
TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, February 25th*, 1944.]

## 103. *Photochemical Reactions. Part VIII. Reaction of Ethylenes with Phenanthraquinone.*

By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

The reactions of phenanthraquinone with styrene, stilbene, αα-diphenylethylene, and triphenylethylene in sunlight are described. The products are probably derivatives of 2 : 3-dihydro-1 : 4-dioxan.

PHOTOCHEMICAL reactions of unsaturated compounds involving the double linkages are known (Berthelot and Gaudechon, *Compt. rend.*, **1910**, **150**, 1169; Stobbe, *Ber.*, **1914**, **47**, 2701; Ciamician and Silber, *Ber.*, **1902**, **35**, 4129), but so far as we are aware the following reaction is without analogy. Under the influence of sunlight, phenanthraquinone reacts readily with styrene, stilbene, αα-diphenylethylene and triphenylethylene, giving probably derivatives of 2 : 3-dihydro-1 : 4-dioxan; *e.g.*,




In all four cases experiments carried out in the dark gave negative results. The photo-products are colourless, and decompose at high temperatures, yielding phenanthraquinone; stilbene and triphenylethylene also have been isolated in the two respective cases. The four photo-products, when treated with sulphuric acid, all yield phenanthraquinone.

### EXPERIMENTAL.

The photo-experiments were carried out in sealed Monax glass tubes (Schlenk tubes) in an atmosphere of carbon dioxide (comp. Part VII, this vol., p. 67).

*Photo-reaction between Phenanthraquinone and Stilbene.*—Phenanthraquinone (1 g.) and stilbene (0·9 g.) in benzene (thiophen-free) (50 c.c.) were exposed to sunlight for 9 days in August, the phenanthraquinone then having dissolved. The benzene was driven off in a vacuum, and the residue washed with cold absolute ethyl alcohol and extracted with hot petroleum (b. p. 100—150°) (phenanthraquinone being difficultly soluble). On cooling (if necessary after concentration), almost colourless crystals were obtained; recrystallised from petroleum (b. p. 100—150°) or xylene, these gave colourless needles, m. p. about 260° (to a red melt) (Found: C, 86·2; H, 5·3. $C_{28}H_{20}O_2$ requires C, 86·5; H, 5·1%). The yield was about 70%.

The *product* (0·5 g.) was treated with concentrated sulphuric acid (3 c.c.) at room temperature and kept overnight. The solution, initially violet and finally brown, was poured on ice, filtered, neutralised with sodium carbonate, and extracted with ether. The extract was dried (anhydrous sodium sulphate) and distilled, leaving phenanthraquinone, identified by mixed m. p.

*Thermal decomposition.* The photo-product was heated in a stream of carbon dioxide in a tube about 25 cm. high at a bath temperature of about 270°. Red-brown fumes were formed and after ½ hour orange drops collected on the walls. After 48 hours, these solidified, forming a mixture of orange and almost colourless crystals. Extraction with hot light petroleum (b. p. 30—50°) removed stilbene, leaving an orange residue of phenanthraquinone. Both products were identified by mixed m. p. determinations after recrystallisation from alcohol.

*Photo-reaction between Phenanthraquinone and Triphenylethylene.*—Phenanthraquinone (1 g.) and triphenylethylene (2·4 g.) in benzene (25 c.c.) were exposed for 4 days in September. The oily residue remaining after removal of the benzene in a vacuum was repeatedly washed with petroleum (b. p. 80—90°) and with absolute ethyl alcohol. Both washings gave, on concentration, colourless crystals, m. p. about 225° (decomp.) after recrystallisation from petroleum (b. p. 80—90°) (Found: C, 87·8; H, 5·2. $C_{34}H_{24}O_2$ requires C, 87·8; H, 5·1%). The *product*, when treated with sulphuric acid, gave an olive-green colour after a few minutes.

*Thermal decomposition.* This was carried out for ½ hour at about 235° (bath temp.) as described above. The mixture of orange crystals of phenanthraquinone and almost colourless crystals of triphenylethylene was separated by means of hot light petroleum (b. p. 30—50°).

*Photo-reaction between Phenanthraquinone and Styrene.*—Phenanthraquinone (1 g.) and freshly distilled styrene (2 c.c.) in benzene (50 c.c.) were exposed for 4 days in October. After removal of the benzene, the residue was treated with light petroleum (b. p. 30—50°); on concentration, the extract gave almost colourless crystals, m. p. about 130° (decomp.) after washing with ether (Found: C, 84·2; H, 5·2. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). The *product*, when treated with sulphuric acid, gave a violet colour after a few minutes. At a bath temperature of about 310° it yielded phenanthraquinone.

*Photo-reaction between Phenanthraquinone and αα-Diphenylethylene.*—Phenanthraquinone (1 g.) and freshly distilled αα-diphenylethylene (1·5 c.c.) in benzene (50 c.c.) were exposed for 16 days in October/November. After the usual treatment, light petroleum (b. p. 30—50°) extracted from the residue a crystalline solid. This was washed with hot ether and recrystallised from petroleum (b. p. 100—150°), giving colourless crystals, m. p. 202—203° (orange melt) (Found: C, 86·4; H, 5·4. $C_{28}H_{20}O_2$ requires C, 86·5; H, 5·1%). The *product* gave no initial coloration with sulphuric acid at the ordinary temperature, but an orange colour was observed immediately at 100°. At a bath temperature of about 230° it decomposed, yielding phenanthraquinone.

FOUAD I UNIVERSITY, ABBASIA, CAIRO. [*Received, March 20th*, 1944.]

## 104. *The Kinetics of the Reaction between Chlorine and Nitric Oxide.*

By Eric M. Stoddart.

Previous experiments have shown that this reaction is considerably influenced by surface conditions, adsorption of the nitrosyl chloride formed during the reaction inhibiting the change. The present work shows that the velocity constant of the reaction ultimately diminishes from experiment to experiment, as well as during each experiment, owing to an ageing effect of the reaction vessel. The original state of the surface cannot be recovered by mere pumping or by baking under vacuum, although the latter procedure is more efficacious than the former. Drying prevents inhibition, and it is concluded that the ageing and inhibitory effects are due to the activated adsorption or chemisorption of nitrosyl chloride on the adsorbed moisture of the wall of the reaction vessel. Such a view would satisfactorily account for the kinetic equation previously employed.

In the previous paper (J., 1940, 823) the data reported for this reaction were obtained from two reaction vessels, one packed and one empty, both of which were used until the results were in agreement amongst themselves. It was thereby clearly indicated that the chlorine–nitric oxide reaction did not obey the termolecular law under the conditions of the experiment, and it seemed that the nitrosyl chloride formed in the reaction was able to inhibit it by being adsorbed on the wall of the reaction vessel; this proves that the reaction is, at least in part, heterogeneous. During this earlier work it had been observed that, when a reaction bulb was first brought into use, it gave comparatively high velocity constants, which diminished as the bulb was used until, eventually, reproducible and concordant results were obtained. This matter has now been carefully examined.

A reaction vessel of soda-glass was sealed into the apparatus in place of the older one (see previous paper). The new vessel was then pumped out for 4 hours by means of a mercury-vapour pump backed by a " Hyvac " pump. The gases were introduced as in the previous work, and the nitrosyl chloride and excess of the reagents were removed by means of an old Geryk pump protected against attack by alkali pellets; the final removal of gas was effected by the Hyvac pump similarly protected, followed by the employment of the mercury-vapour pump acting directly on the apparatus, without such protection, as this would cause considerable restriction to pumping.

The first five experiments carried out with the new vessel gave a steady velocity constant of $12{\cdot}0 \times 10^{-7}$ at 25°; a slight decrease of the velocity constant towards the end of the reaction was noted with the next two experiments, and in the eighth, the decrease was appreciable. The tabulated results of the experiments which followed show that the velocity constants diminish from experiment to experiment as well as during each experiment. After the twentieth experiment, the results were concordant, the initial values of $k$ being $4{\cdot}5 \times 10^{-7}$, in agreement with those of the previous paper. When this bulb was employed for experiments at 15°, the initial value of $k$ was $2{\cdot}2 \times 10^{-7}$, also as previously reported.

This falling off of the initial value of $k$ is presumably due to the adsorption by the wall of some of the nitrosyl chloride, and the pumping carried out between successive experiments is evidently not able to remove the whole of this gas from the wall. There comes a time when conditions are reproducible from experiment to experiment because the state of the wall is always reattained, *i.e.*, the amount of nitrosyl chloride adsorbed by the wall is essentially the same at the beginning of successive experiments, the wall being almost saturated with the gas which is scarcely affected by the pumping.

Another new bulb was employed for the fifth series of experiments, which were carried out at 15°, very similar results being obtained. The first four experiments gave $k = 10{\cdot}6 \times 10^{-7}$ over the whole time range, but further use of the vessel gave results having a distinct fall in the value of $k$ towards the end of each experiment. The initial velocity constant ultimately fell to $2{\cdot}2 \times 10^{-7}$ and then the bulb again gave reproducible experimental data, whether the temperature was at 15° or 25°, *i.e.*, the initial values of $k$ were $2{\cdot}2 \times 10^{-7}$ and $4{\cdot}5 \times 10^{-7}$, respectively.

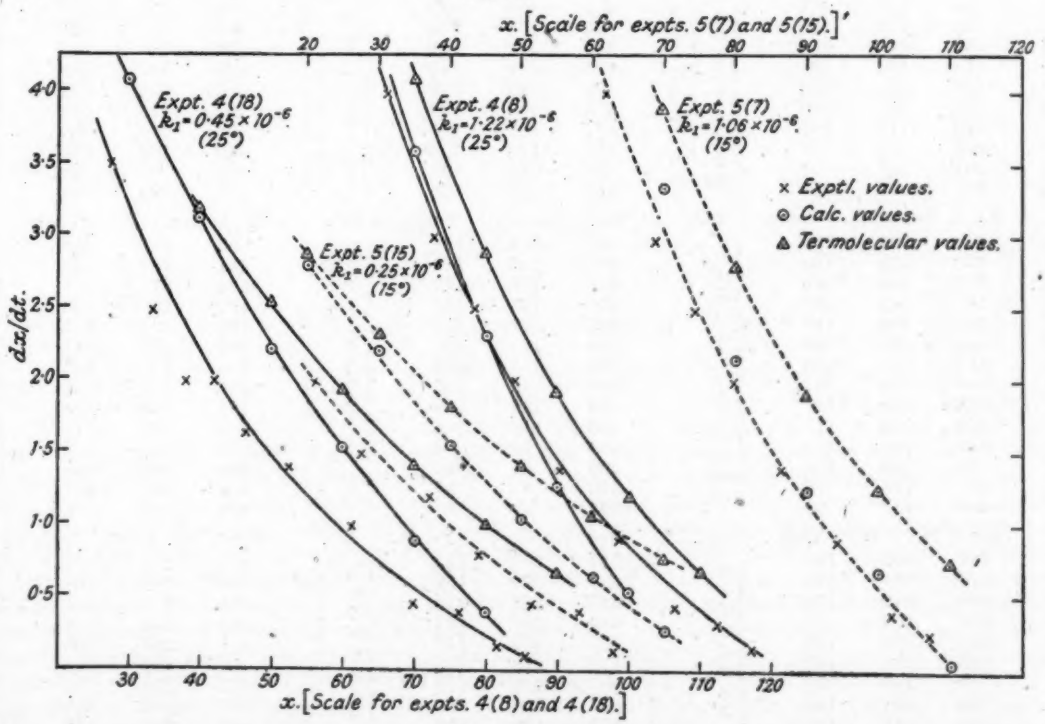
If the theory that not all the adsorbed nitrosyl chloride was removed from the wall by the pumping carried out at the end of each experiment is correct, it was thought that prolonged evacuation by means of a mercury-vapour pump, employing a vapour trap cooled to −80°, together with baking the reaction vessel until the glass collapsed slightly, might achieve complete removal of the adsorbed gas so that the initial value of the velocity constant was restored. The attempt was made on several occasions, but the effect of such treatment was always very small. The bulb used for the fifth series of experiments was treated in this fashion, the apparatus being arranged so that the thermostat bath could be lowered from the apparatus so as to allow the necessary manipulation to be carried out. Expt. 6A followed, and it is seen that baking under vacuum raised the velocity constants but did not effect complete restoration to the termolecular conditions. The bulb was then re-evacuated by means of the mercury-vapour pump for about 6 hours; baking could not be undertaken again with this bulb, since the glass was already considerably distorted. The results of expt. 6B show a general decrease in the velocity constants from those of expt. 6A, and it is clear that pumping alone is not able to effect the results achieved by baking under vacuum.

The bulb used for the fourth series of experiments was now washed out with a little dilute sodium carbonate solution to remove adsorbed nitrosyl chloride, washed with water, and dried in an oven; it was then sealed into place and evacuated by means of the mercury-vapour pump for about 4 hours. Expt. 7A which followed seemed to indicate that the alkali washing had been almost as effective as baking under vacuum. The bulb was baked before expt. 7B, carried out at 15°, whereupon it was again noted that such treatment could increase the value of the velocity constants.

The conditions at the end of each of these and the previous experiments are such as to cause the reaction to proceed very slowly. During the fourth and fifth series of experiments, it had been the practice to admit both the reactants to the reaction vessel at the end of the previous observations, and so measure the rate of reaction employing the poisoned reaction vessel with large concentrations of both reactants. It was found that the reaction velocity was not abnormally increased by the addition of more of the reactants. Rapid evacuation of the reaction vessel and admission of fresh reactants was also tried. It was found that if the evacuation can be completed in about two minutes, the velocity constant of the reaction is extremely low and of the order of that before evacuation. This clearly indicates that the inhibition is due to surface conditions existing towards the end of the reaction period and is in no way due to conditions in the gas phase.

An attempt was also made to see whether the reaction could be inhibited by either of the reactants or the resultant nitrosyl chloride. The reaction vessel was filled with one of the reactants and left for several days to attain equilibrium with the wall; the other reactant was then introduced, and the reaction velocity measured. No effect was detected when nitric oxide was introduced first, but with chlorine the effect was unmistakable. If the chlorine was allowed to enter the vessel about a week before reaction was allowed to take place, a distinct lowering of the velocity constant occurred, as shown in expts. 8A and 8B. It is evident that the adsorption of chlorine can inhibit the reaction to an additional extent, but its effect is very small compared with that of the nitrosyl chloride, since no effect is observed unless the chlorine is allowed to stand in the reaction vessel for several days before the experiment.

FIG. 1.


x. [Scale for expts. 5(7) and 5(15).]
Expt. 4(18) k₁=0·45×10⁻⁶ (25°)
Expt. 4(8) k₁=1·22×10⁻⁶ (25°)
Expt. 5(7) k₁=1·06×10⁻⁶ (15°)
Expt. 5(15) k₁=0·25×10⁻⁶ (15°)
× Exptl. values.
⊙ Calc. values.
△ Termolecular values.
dx/dt.
x. [Scale for expts. 4(8) and 4(18).]

In the previous paper, an equation [(6), *loc. cit.*, p. 830] was deduced in order to account for the decrease of the velocity constant as the reaction proceeded, on the assumption that nitrosyl chloride was slowly and irreversibly adsorbed by the surface, the rate of adsorption being of the same order as the reaction velocity. It was interesting to see whether this equation was obeyed in the present series of experiments. If $k_1$ is taken as the initially observed velocity constant, it is found that nearly all the experiments in the present paper obey the equation satisfactorily, the value of $k_2$ being $1{\cdot}85 \times 10^{-4}$. Extremely close agreement of the experimental results with the equation is found with expts. 4(11), 4(12), 4(15), 5(7), 6A, 6B, and 7A. Fig. 1 shows the values of $dx/dt$ for values of $x$ calculated from the above equation, and also those obtained by assuming the reaction to obey the simple termolecular law, $dx/dt = k_1(a - 2x)^2(b - x)$, as well as the experimental values obtained in expts. 4(8), 4(18), 5(7), and 5(15). The effect of ageing the reaction vessel on the value of $dx/dt$ is well brought out by these curves. When $x = 70$, it is seen that $dx/dt$ is about 3·0 at 15° when a comparatively new reaction vessel is employed, but when the vessel is old enough to give reproducible results, then $dx/dt$ is almost zero for the same value of $x$. The same effect can also be seen by using the value $x = 80$ for the temperature 25°. (The values of $dx/dt$ in each of the successive experiments can be directly compared with one another, since it was arranged that the concentrations of the reactants should be approximately the same in each of these series of experiments.)

(All pressures are recorded in mm. of mercury and times in minutes.)

| Time. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. |
|---|---|---|---|---|
| | Expt. No. 4(8). Temp. = 25°. | | | |
| 0 | 506 | 294 | 212 | |
| 2 | 474 | 230 | 180 | 12·2 |
| 4 | 456 | 194 | 162 | 11·6 |
| 6 | 444 | 170 | 150 | 11·9 |
| 8 | 436 | 154 | 142 | 10·5 |
| 10 | 430 | 142 | 136 | 9·9 |
| 12 | 425 | 132 | 131 | 10·1 |
| 15 | 419 | 120 | 125 | 9·9 |
| 20 | 412 | 106 | 118 | 8·9 |
| 30 | 403 | 88 | 109 | 8·55 |
| 45 | 396 | 74 | 102 | 6·85 |
| 60 | 391 | 64 | 97 | 7·1 |
| 90 | 386 | 54 | 92 | 5·15 |
| 120 | — | — | — | — |
| | Expt. No. 4(12). Temp. = 25°. | | | |
| 0 | 492 | 299 | 193 | |
| 2 | 469 | 253 | 170 | 8·6 |
| 4 | 453 | 221 | 154 | 7·8 |
| 6 | 443 | 201 | 144 | 7·2 |
| 8 | 436 | 187 | 137 | 7·6 |
| 10 | 430 | 175 | 131 | 7·4 |
| 12 | 425 | 165 | 126 | 6·9 |
| 15 | 419 | 153 | 120 | 6·1 |
| 20 | 412 | 139 | 113 | 5·9 |
| 30 | 405 | 125 | 106 | 3·7 |
| 45 | 399 | 113 | 100 | 2·8 |
| 60 | 396 | 107 | 97 | 1·7 |
| 90 | 393 | 101 | 94 | 1·0 |
| 120 | 391 | 97 | 92 | 0·69 |
| | Expt. No. 4(18). Temp. = 25°. | | | |
| 0 | 489 | 306 | 183 | |
| 2 | 475 | 278 | 169 | 4·8 |
| 4 | 465 | 258 | 159 | 4·1 |
| 6 | 458 | 244 | 152 | 4·7 |
| 8 | 453 | 234 | 147 | 4·0 |
| 10 | 449 | 226 | 143 | 3·4 |
| 12 | 445 | 218 | 139 | 3·6 |
| 15 | 440 | 208 | 134 | 3·1 |
| 20 | 433 | 194 | 127 | 2·4 |
| 30 | 423 | 174 | 117 | 2·5 |
| 45 | 416 | 160 | 110 | 1·57 |
| 60 | 410 | 148 | 104 | 1·60 |
| 90 | 405 | 138 | 99 | 0·88 |
| 120 | 402 | 132 | 96 | 0·65 |
| | Expt. No. 5(11). Temp. = 15°. | | | |
| 0 | 489 | 303 | 186 | |
| 2 | 473 | 271 | 170 | 5·1 |
| 4 | 462 | 249 | 159 | 4·4 |
| 6 | 454 | 233 | 151 | 4·5 |
| 8 | 449 | 223 | 146 | 3·6 |
| 10 | 445 | 215 | 142 | 3·1 |
| 12 | 442 | 209 | 139 | 2·7 |
| 15 | 438 | 201 | 135 | 2·4 |
| 20 | 432 | 189 | 129 | 2·9 |
| 30 | 424 | 173 | 121 | 2·0 |
| 45 | 418 | 161 | 115 | 1·4 |
| 60 | 413 | 151 | 110 | 1·2 |
| 90 | 409 | 143 | 106 | 0·57 |
| 120 | 406 | 137 | 103 | 0·45 |
| | Expt. No. 5(15). Temp. = 15°. | | | |
| 0 | 492 | 298 | 194 | |
| 2 | 484 | 282 | 186 | 2·5 |
| 4 | 478 | 270 | 180 | 2·1 |
| 6 | 473 | 260 | 175 | 1·8 |
| 8 | 469 | 252 | 171 | 2·1 |
| 10 | 466 | 246 | 168 | 1·3 |
| 12 | 463 | 240 | 165 | 1·5 |
| 15 | 458 | 230 | 160 | 1·9 |
| 20 | 452 | 218 | 154 | 1·5 |
| 30 | 444 | 202 | 146 | 1·3 |
| 45 | 437 | 188 | 139 | 0·90 |
| 60 | 431 | 176 | 133 | 0·98 |
| 90 | 427 | 168 | 129 | 0·40 |
| 120 | — | — | — | — |

| $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. |
|---|---|---|---|
| Expt. No. 4(9). Temp. = 25°. | | | |
| 497 | 297 | 200 | |
| 468 | 239 | 171 | 11·3 |
| 450 | 203 | 153 | 11·6 |
| 439 | 181 | 142 | 10·3 |
| 430 | 163 | 133 | 11·0 |
| 423 | 149 | 126 | 11·0 |
| 418 | 139 | 121 | 10·1 |
| 412 | 127 | 115 | 9·8 |
| 404 | 111 | 107 | 10·2 |
| 395 | 93 | 98 | 8·6 |
| 388 | 79 | 91 | 6·8 |
| 383 | 69 | 86 | 7·0 |
| 378 | 59 | 81 | 4·9 |
| 375 | 53 | 78 | 4·0 |
| Expt. No. 4(13). Temp. = 25°. | | | |
| 503 | 292 | 211 | |
| 482 | 250 | 190 | 7·5 |
| 468 | 222 | 176 | 7·0 |
| 458 | 202 | 166 | 6·5 |
| 451 | 188 | 159 | 5·5 |
| 445 | 176 | 153 | 5·8 |
| 440 | 166 | 148 | 5·8 |
| 436 | 158 | 144 | 3·7 |
| 430 | 146 | 138 | 3·7 |
| 424 | 134 | 132 | 2·3 |
| 418 | 122 | 126 | 1·9 |
| 415 | 116 | 123 | 1·2 |
| 413 | 112 | 121 | 0·4 |
| 412 | 110 | 120 | 0·2 |
| Expt. No. 5(7). Temp. = 15°. | | | |
| 508 | 309 | 199 | |
| 478 | 249 | 169 | 10·6 |
| 461 | 215 | 152 | 10·4 |
| 450 | 193 | 141 | 9·5 |
| 442 | 177 | 133 | 8·5 |
| 436 | 165 | 127 | 8·2 |
| 431 | 155 | 122 | 8·3 |
| 425 | 143 | 116 | 7·9 |
| 418 | 129 | 109 | 6·8 |
| 409 | 111 | 100 | 6·1 |
| 403 | 99 | 94 | 3·7 |
| 399 | 91 | 90 | 3·3 |
| 396 | 85 | 87 | 1·47 |
| 394 | 81 | 85 | 1·14 |
| Expt. No. 5(12). Temp. = 15°. | | | |
| 511 | 298 | 213 | |
| 497 | 270 | 199 | 4·3 |
| 487 | 250 | 189 | 4·0 |
| 480 | 236 | 182 | 3·3 |
| 475 | 226 | 177 | 2·6 |
| 471 | 218 | 173 | 2·2 |
| 467 | 210 | 169 | 2·8 |
| 462 | 200 | 164 | 2·4 |
| 456 | 188 | 158 | 1·97 |
| 449 | 174 | 151 | 1·44 |
| 443 | 162 | 145 | 0·99 |
| 438 | 152 | 140 | 1·1 |
| 434 | 144 | 136 | 0·44 |
| 431 | 138 | 133 | 0·38 |
| Expt. No. 6A. Temp. = 25°. | | | |
| 504 | 306 | 198 | |
| 484 | 266 | 178 | 6·2 |
| 469 | 236 | 163 | 7·0 |
| 459 | 216 | 153 | 6·6 |
| 451 | 200 | 145 | 5·9 |
| 445 | 188 | 139 | 5·6 |
| 440 | 178 | 134 | 5·3 |
| 434 | 166 | 128 | 5·3 |
| 427 | 152 | 121 | 4·6 |
| 417 | 132 | 111 | 4·2 |
| 409 | 116 | 103 | 3·3 |
| 402 | 102 | 96 | 4·0 |
| 396 | 90 | 90 | 2·3 |
| 392 | 82 | 86 | 2·0 |

| $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. |
|---|---|---|---|
| Expt. No. 4(11). Temp. = 25°. | | | |
| 501 | 295 | 206 | |
| 472 | 237 | 177 | 10·8 |
| 454 | 201 | 159 | 11·0 |
| 442 | 177 | 147 | 11·0 |
| 435 | 163 | 140 | 8·6 |
| 429 | 151 | 134 | 9·1 |
| 425 | 143 | 130 | 6·9 |
| 421 | 135 | 126 | 5·4 |
| 415 | 123 | 120 | 5·9 |
| 407 | 107 | 112 | 5·3 |
| 400 | 93 | 105 | 4·3 |
| 395 | 83 | 100 | 4·2 |
| 392 | 77 | 97 | 1·6 |
| — | — | — | — |
| Expt. No. 4(15). Temp. = 25°. | | | |
| 520 | 309 | 211 | |
| 499 | 267 | 190 | 6·5 |
| 484 | 237 | 175 | 6·5 |
| 474 | 217 | 165 | 5·6 |
| 466 | 201 | 157 | 5·1 |
| 460 | 189 | 151 | 4·7 |
| 455 | 179 | 146 | 4·6 |
| 449 | 167 | 140 | 4·4 |
| 442 | 153 | 133 | 4·0 |
| 432 | 133 | 123 | 3·8 |
| 424 | 117 | 115 | 2·9 |
| 419 | 107 | 110 | 2·4 |
| 415 | 99 | 106 | 1·2 |
| 413 | 95 | 104 | 0·7 |
| Expt. No. 5(10). Temp. = 15°. | | | |
| 503 | 301 | 202 | |
| 481 | 257 | 180 | 7·9 |
| 466 | 227 | 165 | 7·1 |
| 456 | 207 | 155 | 6·8 |
| 448 | 191 | 147 | 6·3 |
| 442 | 179 | 141 | 6·4 |
| 438 | 171 | 137 | 4·9 |
| 432 | 159 | 131 | 5·3 |
| 425 | 145 | 124 | 4·6 |
| 416 | 127 | 115 | 4·1 |
| 410 | 115 | 109 | 2·5 |
| 406 | 107 | 105 | 2·0 |
| 403 | 101 | 102 | 0·87 |
| 401 | 97 | 100 | 0·69 |
| Expt. No. 5(14). Temp. = 15°. | | | |
| 515 | 313 | 202 | |
| 503 | 289 | 190 | 3·0 |
| 494 | 271 | 181 | 2·6 |
| 487 | 257 | 174 | 2·2 |
| 481 | 245 | 168 | 2·6 |
| 477 | 237 | 164 | 1·6 |
| 473 | 229 | 160 | 2·1 |
| 468 | 219 | 155 | 2·5 |
| 462 | 207 | 149 | 1·9 |
| 455 | 193 | 142 | 1·4 |
| 448 | 179 | 135 | 1·1 |
| 443 | 169 | 130 | 0·84 |
| 439 | 161 | 126 | 0·38 |
| — | — | — | — |
| Expt. No. 6B. Temp. = 25°. | | | |
| 613 | 361 | 252 | |
| 588 | 311 | 227 | 4·8 |
| 570 | 275 | 209 | 5·1 |
| 558 | 251 | 197 | 4·0 |
| 549 | 233 | 188 | 4·1 |
| 542 | 219 | 181 | 3·8 |
| 536 | 207 | 175 | 3·7 |
| 528 | 191 | 167 | 3·8 |
| 519 | 173 | 158 | 3·3 |
| 508 | 151 | 147 | 2·7 |
| 501 | 137 | 140 | 1·6 |
| 496 | 127 | 135 | 1·4 |
| 492 | 119 | 131 | 0·66 |
| 489 | 113 | 128 | 0·56 |

| Time. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Expt. No. 7A. | | Temp. = 25°. | | Expt. No. 7B. | | Temp. = 15°. | | Expt. No. 8A. | | Temp. = 25°. | |
| 0 | 503 | 197 | 306 | | 587 | 434 | 153 | | 537 | 327 | 210 | |
| 2 | 492 | 175 | 295 | 5·3 | 571 | 402 | 137 | 3·28 | 525 | 303 | 198 | 3·4 |
| 4 | 484 | 159 | 287 | 4·9 | 560 | 380 | 126 | 2·73 | 515 | 283 | 188 | 3·0 |
| 6 | 478 | 147 | 281 | 4·5 | 551 | 362 | 117 | 2·67 | 507 | 267 | 180 | 2·9 |
| 8 | 473 | 137 | 276 | 4·4 | 544 | 348 | 110 | 2·25 | 499 | 251 | 172 | 3·5 |
| 10 | 469 | 129 | 272 | 4·1 | 538 | 336 | 104 | 2·30 | 493 | 239 | 166 | 3·4 |
| 12 | 465 | 121 | 268 | 4·9 | 533 | 326 | 99 | 2·04 | 489 | 231 | 162 | 2·4 |
| 15 | 460 | 111 | 263 | 4·6 | 527 | 314 | 93 | 1·96 | 483 | 219 | 156 | 2·8 |
| 20 | 454 | 99 | 257 | 4·2 | 520 | 300 | 86 | 1·81 | 476 | 205 | 149 | 2·1 |
| 30 | 447 | 85 | 250 | 3·3 | 510 | 280 | 76 | 1·47 | 463 | 179 | 136 | 2·4 |
| 45 | 441 | 73 | 244 | 2·6 | 502 | 264 | 68 | 1·02 | 450 | 153 | 123 | 2·4 |
| 60 | 437 | 65 | 240 | 2·3 | 497 | 254 | 63 | 0·73 | 443 | 139 | 116 | 1·8 |
| 90 | 434 | 59 | 237 | 1·1 | 494 | 248 | 60 | 0·28 | 438 | 129 | 111 | 0·83 |
| 120 | 432 | 55 | 235 | 0·87 | — | — | — | — | 436 | 125 | 109 | 0·41 |
| | Expt. No. 8B. | | Temp. = 25°. | | Expt. No. 9A. | | Temp. = 25°. | | Expt. No. 9B. | | Temp. = 15°. | |
| 0 | 541 | 276 | 265 | | 549 | 397 | 152 | | 494 | 280 | 214 | |
| 2 | 529 | 252 | 253 | 3·33 | 516 | 331 | 119 | 10·0 | 480 | 252 | 200 | 4·8 |
| 4 | 519 | 232 | 243 | 3·5 | 495 | 289 | 98 | 10·0 | 469 | 230 | 189 | 2·0 |
| 6 | 512 | 218 | 236 | 2·8 | 482 | 263 | 85 | 9·8 | 461 | 214 | 181 | 4·3 |
| 8 | 507 | 208 | 231 | 2·4 | 473 | 245 | 76 | 8·1 | 455 | 202 | 175 | 4·0 |
| 10 | 503 | 200 | 227 | 2·1 | 466 | 231 | 69 | 8·6 | 450 | 192 | 170 | 4·1 |
| 12 | 499 | 192 | 223 | 2·4 | 460 | 219 | 63 | 9·0 | 446 | 184 | 166 | 3·2 |
| 15 | 494 | 182 | 218 | 2·2 | 454 | 207 | 57 | 7·4 | 440 | 172 | 160 | 4·0 |
| 20 | 488 | 170 | 212 | 1·8 | 446 | 191 | 49 | 7·8 | 432 | 156 | 152 | 3·6 |
| 30 | 481 | 156 | 205 | 1·3 | 436 | 171 | 39 | 7·1 | 421 | 134 | 141 | 3·5 |
| 45 | 472 | 138 | 196 | 1·4 | 428 | 155 | 31 | 5·8 | 413 | 118 | 133 | 2·5 |
| 60 | 465 | 124 | 189 | 1·4 | 423 | 145 | 26 | 5·3 | 409 | 110 | 129 | 1·6 |
| 90 | 460 | 114 | 184 | 0·63 | 416 | 131 | 19 | 5·6 | 403 | 98 | 123 | 1·2 |
| 120 | 457 | 108 | 181 | 0·45 | — | — | — | — | 398 | 88 | 118 | 1·5 |

Expt. No. 9c. Temp. = 25°.

| Time. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. | Time. | $p$. | $p_{NO}$. | $p_{Cl_2}$. | $k \times 10^7$. |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 500 | 297 | 203 | | 15 | 439 | 175 | 142 | |
| 2 | 484 | 265 | 187 | 5·2 | 20 | 432 | 161 | 135 | 3·8 |
| 4 | 472 | 241 | 175 | 4·8 | 30 | 422 | 141 | 125 | 3·3 |
| 6 | 463 | 223 | 166 | 4·9 | 45 | 410 | 117 | 113 | 3·8 |
| 8 | 456 | 209 | 159 | 5·0 | 60 | 403 | 103 | 106 | 3·5 |
| 10 | 450 | 197 | 153 | 4·9 | 90 | 395 | 87 | 98 | 2·8 |
| 12 | 445 | 187 | 148 | 4·7 | 120 | 390 | 77 | 93 | 2·6 |
| | | | | 4·3 | | | | | |

If the assumption be correct that the inhibition is due to alteration of the state of the glass surface by adsorption of nitrosyl chloride, pre-treatment with this gas should in time completely mature a new vessel. Nitrosyl chloride, prepared from a mixture of sodium chloride and nitrosylsulphuric acid and condensed in an ice–salt mixture, was dried over calcium chloride and phosphoric oxide before being introduced into the reaction vessel. New vessels were used for each of three experiments, since it is otherwise impossible to disentangle the inhibitions due to the introduced nitrosyl chloride and to the reaction products. After the gas had remained for a given time in the vessel, it was rapidly pumped out and the effect was determined by measuring the reaction velocity. The results were as follows. Expt. 9A: NOCl at 100 mm. for 1 day, $k_1 = 10{\cdot}0 \times 10^{-7}$ at 25°, $k_2$ being low, about $1{\cdot}0 \times 10^{-4}$; expt. 9B: NOCl at 100 mm. for 2 days, $k_1 = 4{\cdot}9 \times 10^{-7}$ at 15°, $k_2 = 1{\cdot}6 \times 10^{-4}$; expt. 9c: NOCl at 350 mm. for 5 days, $k_1 = 5{\cdot}0 \times 10^{-7}$ at 25°, $k_2 = 1{\cdot}7 \times 10^{-4}$.

The effect of drying on the reaction was also studied. Phosphoric oxide was sublimed into the storage and the reaction vessel in a stream of dry oxygen, and after the addition of approximately 10 g. of the oxide to each vessel, the apparatus was sealed, and evacuated by the mercury-vapour pump. After 3 weeks' drying, the storage vessels were filled with their respective gases, and after a further week's drying the velocity of the reaction was studied. The reaction vessel used for the experiment was one which had been thoroughly aged over a long period. It was found that the drying had caused all signs of inhibition to disappear. The velocity constant of the reaction under these conditions was $12{\cdot}6 \times 10^{-7}$ at 25° and $10{\cdot}9 \times 10^{-7}$ at 15°, the reaction obeying the termolecular law during the whole of the experiment. This result was somewhat unexpected, since drying generally inhibits a reaction. Addition of nitrosyl chloride to the reaction vessel a week before the reaction produced no effect whatsoever. A possible explanation is that the inhibition is due to the adsorption of the nitrosyl chloride on the water content of the glass surface. It is well known that the nature of a glass surface depends to a large extent upon its composition and previous history, and in consequence, such surfaces are far from being reproducible; therefore it is likely that different investigators will find differences of behaviour during the course of this reaction. The initial experiments of the present work could easily have been taken as evidence that the reaction was of the homogeneous termolecular type. It was only after a few experiments had been performed that departure from the simple law was detectable.

When a surface adsorbs gas, the physical conditions determine whether activated adsorption or van der Waals adsorption occurs. In the latter case the heat of adsorption is small, the rate of adsorption high, and

the adsorbed gas is readily removed from the surface; when activated adsorption occurs, all these effects are in the opposite sense. Both kinds of adsorption occur simultaneously to some extent in most experiments involving the adsorption of gases.

The tenacity with which the nitrosyl chloride adheres to the surface, as well as the fact that the adsorption isotherm (deduced by assuming van der Waals adsorption) is incapable of quantitatively accounting for the results, indicates that in the present work, the inhibition is due to activated rather than to van der Waals adsorption. Such a view was tentatively put forward in the previous paper, in which it was assumed that the inhibition was due to a slow process of adsorption, thereby enabling an equation to be deduced which satisfactorily follows the course of the reaction.

It is suggested that at the beginning of a series of experiments, the new glass surface contains a considerable amount of adsorbed water, which can in turn adsorb the nitrosyl chloride formed during the reaction, thereby causing inhibition. It is probable that the attachment of the nitrosyl chloride to the adsorbed water is of the chemisorption type and will take place slowly. Thus it is seen that, as experiment succeeds experiment, the adsorbed nitrosyl chloride increases, leading to increasing inhibition. Baking under vacuum will tend to drive off both the adsorbed water and nitrosyl chloride, but it is well known that the adsorbed water is most tenaciously held by glass, and therefore, such treatment is only partly effective in restoring reaction velocity. On the other hand, prolonged drying in a vacuum by phosphoric oxide is an extremely efficient method of removing moisture from glass, and when this has been thoroughly achieved, the tendency for the nitrosyl chloride to be adsorbed is removed, and the reaction becomes termolecular, inhibition disappearing.

Trautz and Schlueter (*Z. anorg. Chem.*, 1924, **136**, 1) found that, according to whether a high concentration of chlorine or of nitric oxide was employed, the velocity constant increased or decreased towards the end of the reaction. Krauss and Saracini (*Z. physikal. Chem.*, 1937, *A*, **178**, 245) suggested that these fluctuations in the termolecular velocity constant were due to experimental error in estimating minute partial pressures towards the close of the experiment. This is probably the case, since in Trautz and Schlueter's experiment 19c, they started with 79·9 mm. of nitric oxide, but the experimental figures show that at least 80·46 mm. were used during the experiment. The departure from the true termolecular conditions led Trautz and Schlueter to suggest that the reaction proceeded in two stages: $NO + Cl_2 \rightleftharpoons NOCl_2$, followed by $NOCl_2 + NO \longrightarrow 2NOCl$. The author has already pointed out that the argument supporting this contention is fallacious, and since their work probably involves experimental errors which account for their conclusions, it seems that this reaction mechanism is without valid support. In these circumstances, it is justifiable to suggest that the reaction mechanism may not be very different from that of the nitric oxide–oxygen reaction, and this view was developed in the earlier paper.

If the temperature coefficient of the reaction is calculated from the initial values of $k$ obtained with new bulbs, then $k_{25°}/k_{15°} = 1{\cdot}13$; but if it is calculated from the initial values of $k_1$ obtained from reaction bulbs which give reproducible results, then $k_{25°}/k_{15°} = 2{\cdot}0$. The former value is in good agreement with the values given by other workers, but it is obvious that the temperature coefficient is largely dependent upon the history of the reaction bulb.

## Experimental.

The general procedure was the same as before, but the arrangement of the tensimeter was improved so as to increase the accuracy of the measurements. The new arrangement is shown in Fig. 2, the procedure being as follows. The reaction vessel, the tensimeter, and its jacket, and the manometer were all evacuated *via* the taps *A* and *D*. All the taps were closed except *C*, and one of the gases was then admitted to the reaction vessel. The pressure in the tensimeter jacket was adjusted by using tap *D* in order to return the needle to its null position. The correctness of the manometer reading was then checked by closing *C* and momentarily opening *B*. The lack of movement in the mercury manometer indicated correct pressure adjustment. This technique connects the reaction vessel to the manometer only, and the volume of the latter was comparatively small. Hence any small movement of the mercury manometer does not introduce a serious error into the measurements. In the earlier procedure, the jacket of the tensimeter was also connected to the reaction vessel and manometer, and since the jacket must possess a considerable volume, the error due to any movement of the manometer would be more serious.

Fig. 2.

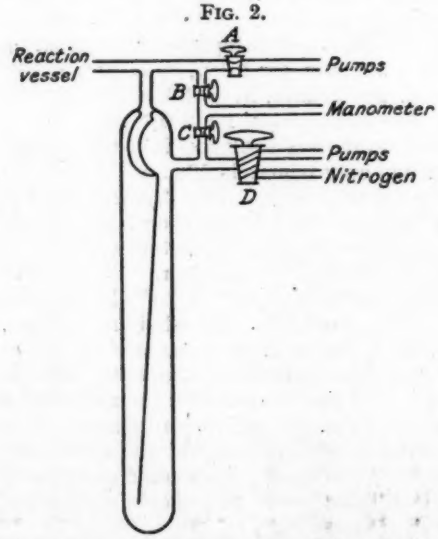
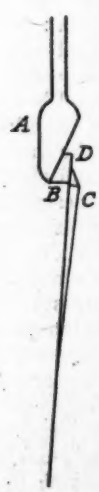



Fig. 3.




The customary method of producing a spoon tensimeter is to blow a thin glass bulb about 1—1½″ in diameter, and then to collapse one half of the bulb; gentle suction produces a "spoon" with the two walls close together. A needle about 18″ long, movement of which is observed by a lens or telescope, is attached to the tip of the spoon. A much better instrument is shown in Fig. 3. A thin bulb is blown so that its length becomes twice its diameter (1½″ and ¾″ respectively are suitable). Half the bulb is collapsed as usual; glass is removed from the collapsed film until it is thin, and then a blowpipe flame is played directly on to the film, which becomes very thin in the middle owing to surface tension thickening the glass towards the cooler edge. It is advisable to stop this thinning process before dark patches (zero interference fringes) appear, otherwise the tensimeter becomes extremely

fragile. If the "spoon" is examined, it will be found that gentle suction causes the tip *B* to move in the opposite direction to the thin membrane at *D*. A thin filament of glass is fused to the membrane at a point which produces the maximum movement (*D*). A U-piece of thin glass is attached to the tip *B*, a fine thread of glass stretched between the tips of the U being the suspension. The needle used is about 18" long, consisting of two filaments of glass bracing one another to produce enhanced rigidity. The needle is attached to the suspension, and an extension of the needle is attached to *D*. The movement of the needle is now due to the combined movements of *B* and *D*, a greater sensitivity than with the orthodox instrument thus being obtained.

For the early work, the orthodox tensimeter was used having a needle movement of 1·2 mm. per 1 mm. of mercury pressure. It was broken early in the present work and replaced by the new type of tensimeter with a movement of 2·1 mm. per 1 mm. of mercury. If these tensimeters are employed in conjunction with a telescope, accurate pressure readings can be obtained. However, in the persent work, the needle movement was observed by the unaided eye in order to make the observations more rapidly.

The zero of these instruments was relatively unaffected by temperature change. A change of 5° had no detectable result on the zero of either instrument, and therefore it was possible to use them without a thermostat. It was noted, however, that when the spoon and its jacket were simultaneously evacuated, the zero shifted as the pressure was lowered, *i.e.*, the null position depended on the pressure being measured. This difficulty was overcome by plotting the zero against the pressure. A curve was used for each instrument, and the zero checked before each experiment.

In the present experiments, it was desired to mix the gases in a definite proportion, irrespective of which gas was first introduced into the reaction vessel. This necessitated some means of adjusting the pressure in the storage vessels, so that the final desired pressure in the reaction vessel could be attained automatically. For this purpose, a pressure adjuster, consisting of a bulb fitted with a three-way tap at the top and attached to a mercury reservoir at the bottom, was inserted into the nitric oxide gas train. The gas was drawn into the bulb at atmospheric pressure, and then released into the storage vessel until the required pressure, indicated by a mercury manometer attached to the vessel, was reached. The chlorine was always stored at atmospheric pressure, as in the previous work, owing to the difficulty of using mercury in this gas train.

The apparatus was calibrated by using air in each storage vessel, so that the pressure adjustments necessary to attain given mixtures of the two gases could be determined. The first gas introduced into the reaction vessel can have its pressure in this vessel adjusted before mixing, by opening tap *A* if the pressure is to be lowered, and by introducing more gas from the train if it is to be raised. In the case of one set of storage and reaction vessels, it was found that if the gas in the reaction vessel introduced from the nitric oxide vessel was adjusted to 200, 300, or 400 mm., then admission of gas from the chlorine vessel, initially at atmospheric pressure, would introduce a further 266, 220, or 170 mm. of gas, respectively. If the gas pressure in the reaction vessel was adjusted to 266, 220, or 170 mm. when gas was first introduced from the chlorine vessel, then the pressure of gas in the nitric oxide vessel must be adjusted to 688, 851, or 1015 mm. respectively in order to introduce 200, 300, or 400 mm. respectively of gas into the reaction vessel. The desired gas mixture could thus be attained at will.

The reaction vessel was shrouded by a thin copper-foil canister, and the connecting tubes and top part of the tensimeter carrying the spoon were wrapped in black paper in order to obviate photochemical reversal. About halfway through the work, the room was blacked out; the manometer and tensimeter needle were then observed by artificial light.

Grants from the Research Fund of the Chemical Society which were used in carrying out this research are gratefully acknowledged.

COLLEGE OF TECHNOLOGY, LEICESTER. [*Received, September 30th*, 1943.]

---

## 105. *An Interpretation of the Sandmeyer Reaction. Part V. The Comparative Behaviour of Cuprous, Cupric, and Ferric Chlorides as Catalysts.*

By HERBERT H. HODGSON and DOUGLAS D. R. SIBBALD.

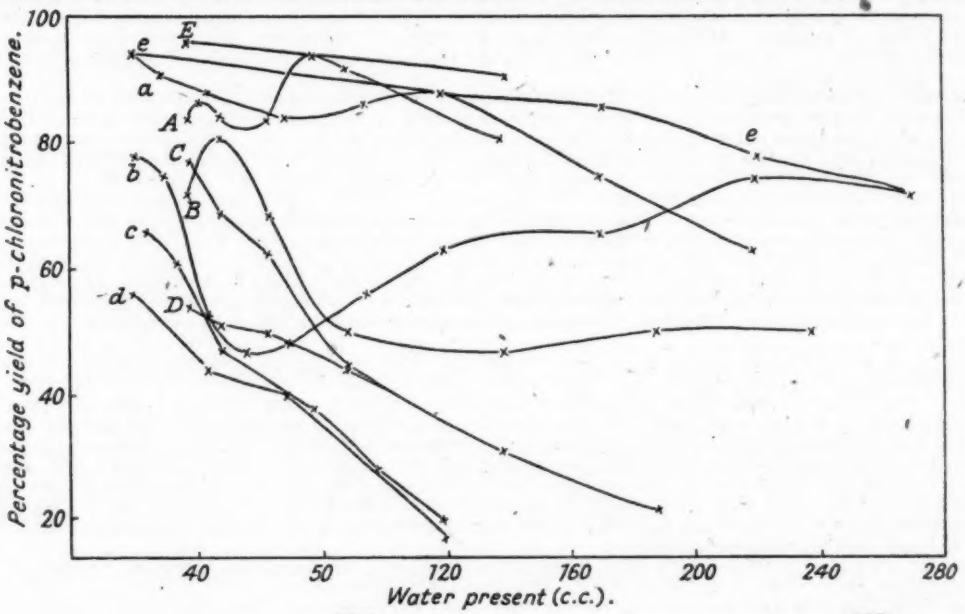
*p*-Nitrobenzenediazonium chloride has been decomposed over a range of hydrochloric acid concentrations with cuprous, cupric, and ferric chlorides as catalysts, and with cuprous and cupric chlorides together. With ferric chloride an almost proportional decrease in yield of *p*-chloronitrobenzene occurs on dilution, whereas cuprous chloride has one maximum at *ca.* 18·6% of acid and cupric chloride has maxima at 26·9% and 4%, the latter after the plot has crossed that for cuprous chloride. The curve for cuprous and cupric chloride in combination approximates to a straight line. These results are discussed from the standpoint of the complex-anion theory.

HODGSON, BIRTWELL, and WALKER (J., 1942, 72) observed that cupric chloride catalysed the decomposition of *p*-nitrobenzenediazonium chloride in somewhat dilute hydrochloric acid solution, and this unexpected result led to the present comparative investigation of the catalytic effects of cuprous and cupric chloride over a wide dilution range. Ferric chloride was also included because of its efficiency in concentrated acid solution (cf. *idem*, this vol., p. 18). From the diagram, which shows the % yield according to the amount of water present, the plot for ferric chloride indicates an almost proportional decrease in yield with dilution, whereas that for cuprous chloride has a maximum at *ca.* 18·6% of acid (see Table I, *a*), and that for cupric chloride has maxima at 26·9% and 4% (see Table I, *b*), the latter after the plot has crossed that for cuprous chloride. When cuprous and cupric chlorides are used in combination (see Table II) the curve is approximately a straight line, the effect of the cuprous chloride being inappreciable at high dilutions; incidentally, the curve for the combination is tangential to the peaks of the cupric chloride curve.

The remarkable increase in activity of cupric chloride at 4% strength suggests the existence of a complex hydrated cupric chloride anion in which the chlorine is much more active than the bound water. This preferential activity of the chlorine may be due to its actual distance from the copper being greater than that of the bound water, as in the known examples of crystalline $K_2CuCl_4.2H_2O$ (cf. Harker, *Z. Krist.*, 1936, **93**, 136; Chrobak, *ibid.*, 1934, **88**, 30; Hendricks and Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 2149). The active amount of this complex would appear to be only slowly changed with increasing dilution.

## Experimental.

*General Procedure.*—The *p*-nitroaniline was diazotised in concentrated hydrochloric acid by addition of solid sodium nitrite, and the mixture kept for 30 mins. Amounts of water and of metallic salts were then added as indicated in the tables, and the reaction carried out by 30 mins.' boiling under reflux. The *p*-chloronitrobenzene formed was removed by steam distillation, dried, and weighed. The mode of addition of the salts was as follows: cuprous chloride (4 g.) immediately after the addition of water; hydrated cupric chloride (6·9 g.) in aqueous solution whenever the amount of water to be added was sufficient for its dissolution; hydrated ferric chloride (10·8 g.) just prior to the addition of water.




| | HCl. 50 c.c. | HCl. 25 c.c. | | HCl. 50 c.c. | HCl. 25 c.c. |
|---|---|---|---|---|---|
| CuCl | A | a | Blank | D | d |
| $CuCl_2$ | B | b | $CuCl + CuCl_2$ | E | e |
| $FeCl_3$ | C | c | | | |

*Note to Tables.*—The added water is calculated on the anhydrous salt in all cases. The yield of *p*-chloronitrobenzene is given to the nearest 0·05 g. and to the nearest 0·5%. Greater accuracy would not alter the conclusions derived from the experimental data.

### Table I.

Yield of *p*-chloronitrobenzene, expressed in g. and %, for the various salts and the blank.

| Water added, g. | Water present, g. | Blank. g. | Blank. % | CuCl, g. | CuCl, % | $CuCl_2$, g. | $CuCl_2$, % | $FeCl_3$, g. | $FeCl_3$, % |
|---|---|---|---|---|---|---|---|---|---|
| (*a*) In these experiments *p*-nitroaniline (2·8 g.) was diazotised with sodium nitrite (2 g.) in hydrochloric acid (50 c.c., *d* 1·16). | | | | | | | | | |
| Nil | 38·0 | 1·8 | 56 | 2·8 | 87·5 | 2·4 | 75 | 2·6 | 81 |
| 2·5 | 40·5 | — | — | 2·8 | 87·5 | 2·3 | 72 | — | — |
| 10·0 | 48·0 | 1·7 | 53 | 2·7 | 84·5 | 2·65 | 83 | 2·2 | 69 |
| 25·0 | 63·0 | 1·6 | 50 | 2·7 | 84·5 | 2·2 | 69 | 2·0 | 62·5 |
| 40·0 | 78·0 | — | — | 3·0 | 94·0 | — | — | — | — |
| 50·0 | 88·0 | 1·4 | 44 | 2·9 | 92·0 | 1·6 | 50 | 1·45 | 45 |
| 100·0 | 138·0 | 1·0 | 31 | 2·6 | 81·0 | 1·5 | 47 | 1·0 | 31 |
| 150·0 | 188·0 | 0·7 | 22 | — | — | 1·65 | 52 | — | — |
| 200·0 | 238·0 | — | — | — | — | 1·65 | 52 | — | — |
| (*b*) Data as for (*a*), but with only 25 c.c. of hydrochloric acid (*d* 1·16).* | | | | | | | | | |
| Nil | 1·9 | 1·8 | 56 | 3 | 94 | 2·5 | 78 | — | — |
| 4·3 | 23·3 | — | — | — | — | — | — | 2·1 | 66 |
| 10·0 | — | — | — | 2·9 | 91 | 2·4 | 75 | — | — |
| 14·3 | 38·3 | — | — | — | — | — | — | 1·95 | 61 |
| 25·0 | 44·0 | 1·4 | 44 | 2·8 | 87·5 | 1·7 | 53 | — | — |
| 29·3 | 48·3 | — | — | — | — | 1·5 | 47 | 1·5 | 47 |
| 50·0 | 69·0 | 1·3 | 41 | 2·7 | 84·5 | 1·55 | 48·5 | — | — |
| 54·3 | 73·3 | — | — | — | — | — | — | 1·2 | 38 |
| 75·0 | 94·3 | — | — | 2·75 | 86·0 | 1·8 | 56 | 0·9 | 28 |
| 100·0 | 119·3 | 0·55 | 17 | 2·8 | 87·5 | 2·0 | 62·5 | 0·65 | 20 |
| 150·0 | 169·0 | — | — | 2·4 | 75 | 2·1 | 66 | — | — |
| 200·0 | 219·0 | — | — | 2·0 | 62·5 | 2·4 | 75 | — | — |
| 250·0 | 269·0 | — | — | — | — | 2·3 | 72 | — | — |

* In this section water was added in portions of 10, 25, 50, 75, 100, etc., g., and to it has been added the water of crystallisation of the salts. This is particularly important when the volume of water is small.

TABLE II.

*Cuprous and cupric chlorides in combination.* Procedure as before, but with cuprous chloride (2·0 g.) and hydrated cupric chloride (3·45 g.).

| With 50 c.c. of HCl (*d* 1·16). | | | | With 25 c.c. of HCl (*d* 1·16). | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$ added, c.c. | Total $H_2O$ present, g. | *p*-Cl·$C_6H_4$·$NO_2$ formed, g. | % | $H_2O$ added, c.c. | Total $H_2O$ present, g. | *p*-Cl·$C_6H_4$·$NO_2$ formed, g. | % | $H_2O$ added, c.c. | Total $H_2O$ present, g. | *p*-Cl·$C_6H_4$·$NO_2$ formed, g. | % |
| Nil | 38·7 | 3·05 | 96 | Nil | 19·7 | 3·0 | 94 | 150 | 169·7 | 2·75 | 86 |
| 40 | 78·7 | 3·0 | 94 | 50 | 69·7 | 2·9 | 91 | 200 | 219·7 | 2·5 | 78 |
| 100 | 138·7 | 2·9 | 91 | 100 | 119·7 | 2·8 | 88 | 250 | 269·7 | 2·3 | 72 |

The authors are indebted to the Charles Brotherton Trust for a Research Scholarship to one of them (D.D.R.S.), and to Imperial Chemical Industries Ltd. (Dyestuffs Division) for the gift of *p*-nitroaniline.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 1st*, 1944.]

---

## 106. *Evidence for the* iso*Nitrile and Nitrile Structures of Hantzsch's Aryl* syn- *and* anti-*Diazocyanides.*

By HERBERT H. HODGSON and EWART MARSDEN.

Hantzsch's aryl *syn*- and *anti*-diazocyanides exhibit differences of chemical reactivity which are accounted for by *iso*nitrile and nitrile structures, *i.e.*, the presence of N–N and N–C bonds in the molecule. Analogy between the *syn*-cyanides and *iso*cyanates is found to be very close. The conversion of the non-coupling *p*-nitrobenzenediazocarbonamide (with its stable C–N bond) by reaction with bromine into an *N*-bromocarbonamide, which will then couple with α- or β-naphthylamine in non-aqueous media, as also with β-naphthol in aqueous-alcoholic and alkaline solution, indicates that the Hofmann reaction has occurred, and that the resulting intermediate diazocyanate with its easily ruptured N–N bond will now couple. The formation of *syn*-cyanides in mineral acid medium finds a parallel in the formation of diazoamino-compounds in acid media of similar strength. The ready rupture of the N–N bond is in accord with chemical experience generally.

IT was obvious when Hantzsch put forward his stereochemical views on the diazohydroxides, diazosulphonates, and diazocyanides, that the great and many chemical differences between the *syn*- and *anti*-compounds were not readily accounted for by mere differences of configuration in space which the fallacious comparison of these compounds with the stereoisomeric oximes had involved. According to Sidgwick ("The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 418), the strongest evidence for Hantzsch's point of view was derived from the study of the diazosulphonates and diazocyanides, and this is to be found in "Die Diazo-Verbindungen" (Hantzsch and Reddelien, 1921), in "The Chemistry of the Diazo-Compounds and Their Technical Applications" (Saunders, 1936), and in papers by Le Fèvre and Vine (J., 1938, 431) and by Stephenson and Waters (J., 1939, 1796).

Recently, however, it was shown by Hodgson and Marsden (J., 1943, 470) that Hantzsch's *syn*- and *anti*-diazosulphonates are not geometrical but structural isomers, *viz.*, diazosulphites and diazosulphonates, respectively, and such a result calls for a re-examination of the position with respect to the *syn*- and *anti*-diazocyanides, despite the apparent confirmation of the stereochemical theory for the structures of these compounds by recent data from dipole-moment measurements (cf. Le Fèvre and Vine, *loc. cit.*).

Stephenson and Waters (*loc. cit.*) ascribe the great chemical reactivity of the *syn*-cyanides in ionising solvents to their partial ionisation, and it is noteworthy that in certain of their decompositions the odour of *iso*nitriles is prevalent. This last fact indicates that the cyanide ion can form a covalent union at its nitrogen atom, and therefore it is reasonable to infer that a like combination can occur between the nitrogens of the cyanide and the diazonium ions when a diazonium salt is treated with potassium cyanide in slightly acid solution. Actually, the addition always results in the formation of a yellow compound initially, which, if the reaction is conducted below −5° persists and the yellow *syn*-cyanide results, whereas if the temperature is above 0° the yellow colour quickly changes through yellow-orange to orange-red and then to red when the stable *anti*-cyanide is formed. In some cases, such as those of *o*- and *p*-chloro- and *p*-bromo-aniline, mixtures of *syn*- and *anti*-diazocyanides are formed above 0° but complete isomerisation takes place when Le Fèvre and Vine's procedure is followed (*loc. cit.*). These experiments support the view of these authors that the *syn*-cyanide is first produced, followed by conversion into the *anti*-isomeride.

One of the difficulties attending the acceptance of the stereoisomerism of the *syn*- and *anti*-diazosulphonates was the ease of coupling of the *syn*-compounds, *i.e.*, the ease of rupture of the bond between the diazo-nitrogen and the $-SO_3Na$ group in the *syn*-, and its impossibility under reasonable conditions in the *anti*-configuration. This difficulty is insurmountable if N–S bonds are postulated in both cases, but the problem receives immediate solution when the difference between the isomerides is ascribed to the ready rupture of an N–O bond in the *syn*- and the non-rupture of an N–S bond in the *anti*-compound. Complete analogies were to be found in the labile diazo-oxides and the stable diazo-sulphides. A similar difficulty arises when a C–N bond is postulated for both *syn*- and *anti*-diazocyanides, whereas the chemical evidence receives adequate explanation when the

*syn*-compounds are held to possess the readily ruptured N–N bond, and the *anti*-diazocyanides the stable C–N link. Further, the difference in bond energies between these two links is 28 kg.-cals./mol. (cf. Pauling, "The Nature of the Chemical Bond," 1940, p, 53), which is of the same order as the 21—22 kg.-cals./mol. reported for the heat of transformation of *p*-bromobenzene-*syn*- into -*anti*-diazocyanide (Le Fèvre and Vine, *loc. cit.*). Also, Stephenson and Waters's experiments (*loc. cit.*), in which the *syn*-cyanide instantly reacts with silver nitrate, find a parallel in the formation of Prussian-blue when the *syn*-cyanide (but not the *anti*-cyanide) is treated successively with sodium hydroxide, ferrous sulphate, hydrochloric acid, and ferric chloride. Analogies are to be found of the readily ruptured N–N link in the diazoamino-compounds and in the transformations of hydrazo-compounds into benzidines and semidines. The fact that the *syn*-cyanide requires to be formed in weakly acid solution also finds a parallel in the care with which diazotisation must be conducted, even in mineral acid solution, in order to avoid formation of diazoamino-compounds which have comparable, and in the case of *pp'*-dinitrodiazoaminobenzene superior, stability to the *syn*-diazocyanides in mineral acid of similar concentration.

Temperature appears to be of prime importance in bringing about the transformation of *syn*- into *anti*-diazocyanide, which takes place fairly rapidly with the *p*-nitro- and the *p*-chloro-benzene derivative, even in ethereal solution at about 0°.

When the *o*- and *p*-chloro-, *o*- and *p*-bromo-, and *p*-nitro-*syn*- and -*anti*-benzenediazocyanides are treated with methylmagnesium iodide in dry ether, orange-red complexes are formed, the *anti*- having a deeper red colour than the *syn*-complex, and subsequent decomposition of these complexes by iced 2N-sulphuric acid gives acetaldehyde from the *syn*- but not from the *anti*-complexes. To ensure that no *syn*-diazocyanide remained unisomerised in the experiments with the *anti*-compounds, since *o*-chloro- and *o*-bromo-benzene-*syn*-diazocyanides isomerise slowly, all the isomerisations were separately carried out in benzene solution according to Le Fèvre and Vine's directions (*loc. cit.*) before reaction with the Grignard reagent in dry ethereal solution. The yields of acetaldehyde, as determined by the 4-nitro- and the 2 : 4-dinitro-phenylhydrazones, were of the order of 20%, and we are of opinion that some isomerisation of *syn*- to *anti*-compound takes place before the formation of the complex since the *anti*- appeared to be formed rather more rapidly than the *syn*-complexes. Ths reaction with the Grignard reagent finds an analogy in the *iso*nitriles, which also give aldehydes under like conditions (cf. Sidgwick, *op. cit.*, p. 319), but the *anti*-diazocyanides when treated with phenylmagnesium bromide yield eventually considerable amounts of carbylamine, which suggests that the initial complex may be a mixture and contain a component of structure NR:N·C(MgBr):NPh, which in the subsequent decomposition might be expected to give phenyl *iso*nitrile. On analogy also, the m. p.'s of the *syn*-diazocyanides are lower than those of the *anti*-isomerides and so correspond with the lower b. p.'s of the organic *iso*cyanides than of the isomeric nitriles, and the ready ability of the *syn*-diazocyanides to form double compounds with metallic cyanides finds a parallel in the similar double-cyanide formation by organic *iso*cyanides. This property of forming double cyanides is lacking in the *anti*-diazocyanides. The course of the Grignard reactions with the *syn*-diazocyanides would therefore appear to be best represented by the following sequence of stages based on the assumption of an *iso*nitrile structure :

$$C_6H_4R\cdot N:N\cdot\overset{+}{N}:\overset{-}{C} + MgIMe \longrightarrow C_6H_4R\cdot N:N\cdot N:CMe\cdot MgI \xrightarrow[\text{Hydrolysis}]{} C_6H_4R\cdot N:N\cdot N:CHMe \xrightarrow[\text{hydrolysis}]{\text{Further}} CH_3\cdot CHO$$

The ease of resonance of the non-polar nitrile structure has been pointed out by Stephenson and Waters (*loc. cit.*) as comparable with that of azobenzene, and this is shown by the deep red colour of the *anti*-diazocyanides which is similar to that of azobenzene, whereas the presence of the dipolar *iso*nitrile group in the *syn*-diazocyanide, with the consequent electronic strain imposed on the molecule, would account for the yellow colour of these compounds when formed initially. We suggest that the orange colours reported for the solid *syn*-diazocyanides provide evidence that a certain amount of isomerisation has taken place, a circumstance perhaps reflected in their low m. p.'s. Such isomerisation is so prone to take place, particularly in those compounds on which Hantzsch based his theory, that he must always have been dealing with a mixture of the two isomerides as in the case of his *syn*-diazosulphonates.

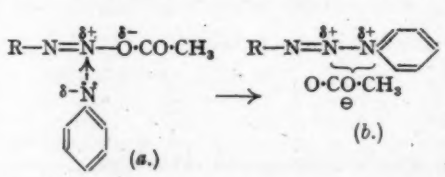
The ease of rupture of the N–N bond is also shown in the facile coupling of the diazo*iso*cyanates, NR:N·NCO. Both *syn*- and *anti*-*p*-nitrobenzenediazocyanides on hydrolysis give the same diazocarbonamide (Hantzsch and Schulze, *Ber.*, 1895, **28**, 666), $NO_2\cdot C_6H_4\cdot N:N\cdot CO\cdot NH_2$, which is a relatively stable substance and does not couple with alkaline β-naphthol, thereby indicating the resistance to rupture of the C–N bond. When, however, this carbonamide is treated with bromine in a dry, neutral solvent such as chloroform or benzene, or in glacial acetic acid, an orange-red substance is precipitated, which is probably a perbromide since it rapidly loses bromine in the air, and changes to a comparatively stable yellow ***substance*** whose analysis and chemical behaviour correspond to $NO_2\cdot C_6H_4\cdot N:N\cdot CO\cdot NHBr,HBr$. This *N*-bromocarbonamide when added to a solution of α- or β-naphthylamine in chloroform or benzene rapidly couples to give *p*-nitrobenzeneazo-α- or -β-naphthylamine, but will not do so with a chloroform or benzene or absolute alcoholic solution of β-naphthol. If, however, aqueous-alcoholic β-naphthol is employed, and of course alkaline β-naphthol, coupling occurs at once to give *p*-nitrobenzeneazo-β-naphthol.

The mechanism of the naphthylamine couplings with the *N*-bromocarbonamide undoubtedly involves that of the well-known Hofmann rearrangement (*Ber.*, 1882, **15**, 407), whereas the coupling with β-naphthol requires intermediate hydrolysis of the *N*-bromocarbonamide to the hydroxamic acid, $NO_2\cdot C_6H_4\cdot N:N\cdot CO\cdot NH\cdot OH$,

followed by the Lossen rearrangement (*Annalen*, 1872, **161**, 347). In both cases the formation of a diazo*iso*cyanate with its weak N–N link must precede coupling. The fact that the naphthylamine couplings take place in a medium where hydrolysis is precluded, affords evidence against the diazonium ion coupling theory of Wistar and Bartlett (*J. Amer. Chem. Soc.*, 1941, **63**, 413) and Hauser and Breslow (*ibid.*, p. 418), and in favour of the polarisation theory (cf. Hodgson, *J. Soc. Dyers Col.*, 1942, **58**, 228). It is of interest that both acetamide (Hofmann, *loc. cit.*) and benzamide (Laurent, Gmelin's "Handbuch der Organischen Chemie," 1848—1870, **3**, 115) form labile compounds with bromine without apparent replacement of hydrogen, whereas such replacement has undoubtedly occurred in the *p*-nitrobenzenediazo-*N*-bromocarbonamide, since free bromine is not evolved from it, whereas it reacts with water partly to regenerate the unbrominated carbonamide and partly to form the hydroxamic acid which undergoes the Lossen rearrangement and so gives a compound, *viz.*, the *iso*cyanate, which has coupling properties. In addition, a labile compound with bromine, such as those described by Laurent and Hofmann, could hardly be expected to couple with β-naphthol in aqueous alcohol. Further evidence of the reactivity of the diazo*iso*cyanates is afforded by the formation of 4 : 4′-dinitrodiazoaminobenzene when neutral *p*-nitrobenzenediazonium sulphate is treated with potassium cyanate and the mixture kept overnight, the almost quantitative yield indicating that the *p*-nitrobenzenediazo*iso*cyanate first formed must have decomposed intermediately to give *p*-nitroaniline which has then reacted with unchanged diazonium sulphate to give the diazoamino-compound. That an *iso*cyanate is formed has an analogy in the production of phenyl *iso*cyanate when benzenediazonium salts react with potassium cyanate (Gattermann and Canzler, *Ber.*, 1890, **23**, 1225; 1892, **25**, 1086), and in the striking fact that only the *iso*cyanates are known of the two possible series of esters of cyanic acid. All our attempts to isolate a diazocyanate or *iso*cyanate by treating neutral *p*-nitrobenzenediazonium chloride with potassium or silver cyanate were frustrated by the facile decomposition of the resulting diazo-compound. An attempt to crystallise the *N*-bromocarbonamide from ethyl alcohol afforded *p*-bromobenzene, showing that the hot alcohol had brought about the Hofmann rearrangement, and that the resulting diazo*iso*cyanate had reacted with the liberated hydrobromic acid in the usual manner.

An explanation of Pieroni's coupling reactions (*Gazzetta*, 1922, **52**, ii, 32) with his so-called azoxycarbonamides may be afforded by the above data, *viz.*, that the azoxycarbonamides, which were prepared from the diazocarbonamides by oxidation with hydrogen peroxide, are really the isomeric hydroxamic acids of formula $NR{:}N{\cdot}CO{\cdot}NH{\cdot}OH$ and not $NR{:}N{\cdot}CO{\cdot}NH_2$, and that with alkaline β-naphthol they undergo the Lossen rearrangement with subsequent coupling of the diazo*iso*cyanate and the β-naphthol; hydrolysis of the *iso*cyanate may of course take place before coupling, although direct coupling is recorded above in non-hydrolytic solvents. Incidentally, Oliveri-Mandalà (*Gazzetta*, 1922, **52**, i, 107) found that the oxidation of benzamide and toluamide by hydrogen peroxide gave the corresponding hydroxamic acid.

The great reactivity of the *syn*-diazocyanides is paralleled by the action of pyridine in promoting the coupling reaction (see numerous patents). One type of an azo-dye is made by coupling a diazo-compound with an aminonaphthalene, diazotising the amino-compound, coupling again, and so building up a chain of aromatic nuclei united by azo-links. This process cannot be continued indefinitely owing to the decreasing stability of the ever-enlarging diazo-compound, and difficulties are encountered which increase after the third repetition of the cycle. It would appear that the promoting action of the pyridine, whereby the above chain can be extended, is due to its reaction with the diazo-compound (*a*), an acetate in the usual examples, with formation of a kation (*b*), which will temporarily prevent decomposition of the unstable diazo-compound, but which, having like adjacent charges (cf. Pauling, *op. cit.*, pp. 109, 210), will subsequently decompose in contact with a molecule of the second amino-component to give an azo-compound. The ease and mechanism of coupling of the *syn*-diazocyanides which occurs in chloroform or alcoholic solution with α-naphthylamine or β-naphthol can also be attributed to the like adjacent charges, on the assumption that the *syn*-diazocyanides have the *iso*nitrile structure, $NR{=}N{-}\overset{+}{N}{\equiv}\overset{-}{C}{:}$.




*Conclusions.*—(1) Hantzsch's stereo-formulation of the aryl *syn*-diazocyanides will not explain (*a*) the formation of complexes with methylmagnesium iodide or phenylmagnesium bromide, in dry ethereal solution, leading eventually on hydrolysis to acetaldehyde and benzaldehyde, respectively, and the non-formation of an aldehyde with corresponding reactions of the *anti*-isomerides; (*b*) ionisation; (*c*) the ease with which the link between the diazo- and the cyanide group is ruptured in non-ionising solvents and also in coupling with α-naphthylamine and β-naphthol in chloroform and alcohol; (*d*) the great difference in colour, indicating strain in the *syn*-compound such as the presence of a dipole would confer; (*e*) the contrasting great stability of the *anti*-isomerides.

(2) Hantzsch's formulation of the *anti*-diazocyanides is correct and in accord with electronic demands. (3) The parallel behaviour of the diazo*iso*cyanates and the *syn*-diazocyanides is explained by the easy rupture of an N–N link, whereas the stability of the *anti*-diazocyanides and the diazocarbonamides is due to the resistance to rupture of a C–N link. (4) The colours of both *syn*- and *anti*-diazocyanides indicate covalent links between the diazo- and the $-\overset{+}{N}{\equiv}\overset{-}{C}{:}$ and $-C{\equiv}N{:}$ groups, respectively. (5) The ease of rupture of the N–N link is in accord with Pauling's theory of adjacent charges and of the inferior strength of the N–N compared with the

C–N link. (6) Chemical reactions in general are entirely in favour of Orton's view (J., 1903, **83**, 796) that the *syn*- and *anti*-diazocyanides are the diazo*iso*nitriles and diazonitriles respectively.

(7) Le Fèvre and Vine's dipole-moment data (*loc. cit.*), which, with suitable assumptions, have been shown to support Hantzsch's views on the stereoisomerism of the *syn*- and *anti*-diazocyanides, are, in a broad qualitative way, not really antagonistic to the structural formulation. Since the halogenobenzene-*anti*-diazocyanides have greater resultant dipole moments than their *syn*-isomerides, this can be held to indicate a subtractive effect when the —C≡N: group is changed to the —$\overset{+}{\text{N}}\equiv\overset{-}{\text{C}}$: group; when, therefore, the halogen is replaced by the nitro-group, as in the *p*-nitrobenzene-*syn*- and -*anti*-diazocyanides, with consequent reversal in sign of the mesomeric dipolar halogen to that of the dipolar nitro-group, a change in resultant effect in favour of the *syn*-isomerides is to be expected. Resonance will probably account for numerical details.

## Experimental.

*syn*-Diazocyanides were prepared from *o*-chloro-, *p*-chloro-, *o*-bromo-, *p*-bromo-, and *p*-nitro-anilines by the procedure of Le Fèvre and Vine (*loc. cit.*), the temperature being kept at −10°. Above −5°, isomerisation appears to occur in all cases to a certain extent. The drying procedure before the treatment with the Grignard reagent was that described by Stephenson and Waters (*loc. cit.*). Isomerisation of the *syn*- to the *anti*-diazocyanides was carried out in benzene solution according to Le Fèvre and Vine (*loc. cit.*).

*Reaction of the* syn- *and* anti-*Diazocyanides with Methylmagnesium Iodide.*—A solution of the diazocyanide (0·02 g.-mol.) in dry ether was added gradually at 0° to methylmagnesium iodide (0·02 g.-mol.) prepared in dry ether. The orange complex was formed immediately, and after being kept at 0° for 15 mins., the mixture was boiled for 15 mins., cooled, and decomposed by 2N-sulphuric acid containing ice. The layers were separated, and the ethereal portion extracted several times with water, the extracts being added to the sulphuric acid portion; this mixture was filtered and treated (*a*) with 2 : 4-dinitrophenylhydrazine dissolved in 2N-sulphuric acid or (*b*) with 4-nitrophenylhydrazine hydrochloride dissolved in water. The resulting hydrazones from the *syn*-compounds were dried and weighed, then crystallised and identified as the hydrazone of acetaldehyde. *p*-Nitrobenzene-*syn*- and -*anti*-diazocyanides were also brought into reaction with phenylmagnesium bromide, and the benzaldehyde obtained from the *syn*-compound identified by conversion into the 2 : 4-dinitro- and 4-nitro-phenylhydrazones. The yields of acetaldehyde were about 20% on the weight of the *syn*-diazocyanide taken.

*Bromination of* p-*Nitrobenzenediazocarbonamide.*—A solution of the carbonamide (1 g.) (prepared according to Hantzsch and Schulze, *loc. cit.*) in glacial acetic acid (25 c.c.) was kept at 0—5° and treated with bromine (3 g.); at higher temperatures nitrogen was evolved immediately. After 2 hours, the crystalline, orange-red product, which had separated in needles, was filtered off, washed with chloroform, and dried on filter-paper. Bromine was evolved, and, after its cessation, a yellow crystalline compound remained (1·3 g.) which appeared to be the *hydrobromide* of p-*nitrobenzenediazo*-N-*bromocarbonamide*, m. p. *ca.* 81° (decomp.) (Found: Br, 45·5. $C_7H_5O_3N_4Br,HBr$ requires Br, 45·2%). The same sequence of products was obtained by bromination in chloroform. This *N*-bromocarbonamide (1 g.), when suspended in cold water (30 c.c.) and aerated for 1—1½ hours, regenerated some of the original *p*-nitrobenzenediazocarbonamide (0·2 g.), which was filtered off; when the filtrate was added to alkaline β-naphthol, *p*-nitrobenzeneazo-β-naphthol was precipitated. The coupling reactions of this *N*-bromocarbonamide are described on p. 396. When the *N*-bromo-compound (1 g.) was decomposed in the cold with 20% aqueous sodium hydroxide (20 c.c.), an immediate darkening in colour occurred with rapid evolution of nitrogen and carbon dioxide; the solution on acidification with acetic acid gave 4 : 4′-dinitrodiazoaminobenzene (0·25 g.), m. p. after recrystallisation from alcohol, and mixed m. p. with authentic specimen, 226° (Found: N, 24·5. Calc.: N, 24·4%).

*A New Preparation of* 4 : 4′-*Dinitrodiazoaminobenzene.*—*p*-Nitrobenzenediazonium sulphate (2 g.) was dissolved in water (7 c.c.), and the filtered solution mixed at 0° with powdered potassium cyanate (0·8 g.); an immediate evolution of nitrogen and carbon dioxide took place together with some lachrymatory substance, doubtless *p*-nitrobenzene *iso*cyanate. After the mixture had been kept for one hour, the light yellow precipitate of 4 : 4′-dinitrodiazoaminobenzene (1·7 g.) was filtered off and crystallised from alcohol; m. p. and mixed m. p. with authentic specimen, 226°.

The authors thank Imperial Chemical Industries Limited (Dyestuffs Division) for gifts of chemicals.

Technical College, Huddersfield. [*Received, April 6th*, 1944.]

---

## 107. *The Preparation and Diazotisation of* p-*Aminomonomethylaniline.*

By Herbert H. Hodgson and Ewart Marsden.

Hantzsch's failure to diazotise *p*-aminomonomethylaniline was apparently due to the presence of *p*-phenylenediamine in his initial material, which originated from the fission of the methyl group during the reduction of *p*-nitrosomonomethylaniline in acetic acid solution. A new method of reduction with iron and ferrous ammonium sulphate (or ferrous sulphate) in neutral solution is now described, in which the rupture of the methyl group has been avoided, and this method has proved to be of general service. The *p*-aminomonomethylaniline when treated with nitrous acid is first diazotised and subsequently nitrosated at the methylamino-group.

Hantzsch (*Ber.*, 1902, **35**, 896) stated that *p*-aminomonomethylaniline cannot be diazotised (cf. also Ayling, Gorvin, and Hinkel, J., 1941, 614), and Saunders ("The Aromatic Diazo-Compounds and their Technical Applications," E. Arnold & Co., London, 1936, p. 63) accepts this report in a discussion on the influence of substituents on the stability of diazonium compounds, concluding that a monoalkylamino-group in the para-position to the diazo-group will decrease the stability of the diazotised amine to such an extent that it decomposes as a primary aliphatic amine does when treated with nitrous acid.

In D.R.-P. 154,336 (cf. A., 1904, 1063) the diazotisation of *p*-aminomonoalkylanilines in general, and of the methyl compound in particular, was reported, but it was accompanied by nitrosation at the *p*-alkylamino-group, since 2 mols. of nitrous acid were employed per mol. of the *p*-aminomonoalkylaniline taken; the *p*-diazo-

derivative of the nitrosoamine formed, coupled normally with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid in the presence of sodium hydroxide, carbonate, or acetate. This patent was apparently overlooked by the above authors.

It is not stated in the patent how the *p*-aminomonomethylaniline was prepared, but Hantzsch, who made it by reduction of *p*-nitrosomonomethylaniline with zinc and acetic acid, reported that his attempted diazotisation of it only resulted in a vigorous evolution of nitrogen. When Hantzsch's directions for the preparation of *p*-aminomonomethylaniline were followed, however, a copious evolution of methyl acetate was obtained, and similar reductions by metals and acids, of both *p*-nitroso- and *p*-nitro-monomethylaniline, always resulted in a partial expulsion of the methyl group with formation of *p*-phenylenediamine. The latter compound has recently been reported as a catalyst for the decomposition of diazonium salts. Golossenki (*Chem. Zentr.*, 1937, **108**, II, 112) determines these by decomposing them in the cold with *p*-phenylenediamine, an operation requiring 5—10 mins. This observation has been confirmed by us, and we also attribute the loss in yield of dye, when diazo-compounds are coupled with *m*-phenylenediamine containing the *o*-isomeride as impurity, to a similar catalytic decomposition.

We find that fission of the methyl group may be avoided by reducing *p*-nitroso- or *p*-nitro-monomethylaniline in neutral suspension in boiling water with iron powder (preferably as pin dust), and with a small amount of ferrous ammonium sulphate (or ferrous sulphate) present; reduction takes place smoothly with passage of *p*-aminomonomethylaniline into solution, where, when it is treated with nitrous acid, none of the frothing and decomposition described by Hantzsch is experienced.

In the patent (*loc. cit.*) no indication is given as to whether diazotisation precedes nitrosation or *vice versa*, or whether both occur simultaneously, and it is now established that diazotisation precedes nitrosation, since when less than 1 equiv. of sodium nitrite is employed only diazotisation occurs. This fact was established by adding the diazo-mixture to excess of dilute sodium hydroxide, filtering off the precipitated excess of *p*-aminomonomethylaniline, and then coupling the diazo-hydroxide left in the filtrate with β-naphthol to form p-N-*methylaminobenzeneazo*-β-*naphthol*, which was shown to be identical with the compound prepared by hydrolysis of authentic *p*-*N*-acetomethylamidobenzeneazo-β-naphthol. Also, when the solution of *p*-aminomonomethylaniline in dilute sulphuric acid was treated with less than 1 equiv. of sodium nitrite, followed by potassium iodide, *p*-iodomonomethylaniline was formed, but owing to difficulties of crystallisation it was converted by treatment with nitrous acid into the readily crystallisable p-*iodo*-N-*nitrosomethylaniline*. Similarly, when deficiency diazotisation was carried out in hydrochloric or hydrobromic acid and followed by the corresponding Sandmeyer reaction, *p*-chloro- and *p*-bromo-monomethylanilines were formed, respectively, and, being liquids, were converted into the solid *N*-nitroso-compounds for identification. Generally, the *N*-nitrosated unlike the free *N*-methylamino-compounds crystallise well from the ordinary solvents.

Since *p*-aminomonomethylaniline can be diazotised independently of attendant nitrosation, the theoretical arguments developed by Saunders *et al.* (*loc. cit.*) based on *non*-diazotisation become invalid. It was to be anticipated that diazotisation would precede nitrosation, since both processes can be regarded from one standpoint as involving condensation of the hydroxyl group of the nitrous acid with hydrogen, and the electron-repelling methyl group would tend to bind the condensing hydrogen of the methylamino-group more firmly than the corresponding hydrogen in the unsubstituted amino-group.

The reduction method referred to above is to be preferred for general purposes to the ordinary Béchamp process with iron and dilute acid, especially as the very objectionable odours inseparable from the latter procedure are avoided.

## Experimental.

*Reduction of* p-*Nitromonomethylaniline.*—A mixture of the nitro-compound (3 g.), pin dust (10 g.), and ferrous ammonium or ferrous sulphate (1 g.) was boiled with water (100 c.c.) under reflux for one hour, ammonia (1 c.c., *d* 0·88) added to precipitate iron, and the solution filtered. The almost colourless hot filtrate darkens on exposure to air, but deposits leaves of white *p*-aminomonomethylaniline in an atmosphere of carbon dioxide, m. p. 35·5° (Willstätter and Pfannenstiehl, *Ber.*, 1905, **38**, 2269, give m. p. 35·5°) (Found: N, 23·1. Calc.: N, 22·95%). The solution was coloured an intense red by a trace of ferric chloride but was then decolorised by hydrochloric acid, to be subsequently turned blue by addition of hydrogen sulphide water. The *picrate* was formed when the hot solution of the base (prepared as above) was filtered into a saturated solution of picric acid in water or alcohol; it crystallised from ethyl alcohol in long, slender, yellow parallelepipeds, m. p. 206° (Found: N, 20·1. $C_{13}H_{13}O_7N_5$ requires N, 19·9%). The period of one hour required for complete reduction in this example may have to be altered for other nitro-compounds.

*Preparation of* p-N-*Methylaminobenzeneazo*-β-*naphthol.*—*p*-Nitro-*N*-methylacetanilide (4 g.) was reduced as above, and the filtered solution of the *p*-amino-*N*-methylacetanilide acidified with hydrochloric acid (20 c.c., *d* 1·16), diazotised, the solution of the diazonium compound run into alkaline β-naphthol, and the precipitated *p*-*N*-acetomethylamidobenzeneazo-β-naphthol removed; it crystallised from 50% aqueous pyridine in red plates, m. p. 139° (Morgan and Grist, J., 1918, **113**, 691, give m. p. 139°) (Found: N, 13·1. Calc.: N, 13·1%), which gave a blue-red colour with concentrated sulphuric acid that changed to a reddish-scarlet on dilution with water. This acetyl compound was hydrolysed by 2 hours' boiling with a solution of hydrochloric acid (1 part, *d* 1·16) and ethyl alcohol (2 parts), then filtering it hot; the filtrate on cooling deposited the *hydrochloride* of p-N-*methylaminobenzeneazo*-β-*naphthol* in red micro-plates, m. p. 197—202° (Found: N, 13·6; HCl, 11·6. $C_{17}H_{15}ON_3$,HCl requires N, 13·4; HCl, 11·6%). This salt on boiling with 50% aqueous pyridine gave the *base*, which separated from the filtered solution on cooling in deep blue-black, spear-like crystals, m. p. 123° (Found: N, 15·3. $C_{17}H_{15}ON_3$ requires N, 15·2%), and gave a bluish-red colour with concentrated sulphuric acid which changed through scarlet and orange to yellow on dilution with water.

*Preparation of* p-N-*Nitrosomethylaminobenzeneazo*-β-*naphthol.*—A solution of *p*-aminomonomethylaniline (prepared as above) was acidified by either hydrochloric or sulphuric acid and then treated with just more than 2 equivs. of sodium nitrite; the excess nitrous acid was removed by urea, and the mixture then stirred into alkaline β-naphthol; p-N-*nitroso*-

*methylaminobenzeneazo-β-naphthol* was precipitated, removed, and dissolved in boiling pyridine, from which it separated on cooling in red, spearlike needles, m. p. 178° (Found: N, 18·5. $C_{17}H_{14}O_3N_4$ requires N, 18·3%), which gave a brilliant red-violet colour with concentrated sulphuric acid, changing through reddish-yellow to pink on dilution with water.

*Experimental Proof that* p-*Aminomonomethylaniline when treated with Nitrous Acid was diazotised before being nitrosated.*—The aqueous solution obtained by the reduction (as above) of *p*-nitromonomethylaniline (6 g.) was added to iced hydrochloric acid (20 c.c., *d* 1·16), and the mixture treated gradually at 0° with an aqueous solution of sodium nitrite (1·0 g.). The nitrite (now much less than 1 equiv.) reacted at once, and no positive test could be obtained with starch–potassium iodide paper. The solution was then stirred into excess of 10% aqueous sodium hydroxide and filtered immediately from the precipitated *p*-aminomonomethylaniline; the filtrate was stirred into alkaline β-naphthol, and *p*-*N*-methylaminobenzeneazo-β-naphthol was precipitated, removed, and crystallised from 50% aqueous pyridine, being obtained in deep blue-black, spearlike crystals, m. p. and mixed m. p. with the authentic compound above, 123° (Found: N, 15·3%). This precipitate was redissolved in mineral acid, treated with excess of sodium nitrite, and the solution run into alkaline β-naphthol; *p*-*N*-nitrosomethylaminobenzeneazo-β-naphthol separated and crystallised as above, m. p. and mixed m. p. with previous specimen, 178° (Found: N, 18·4%).

Three separate solutions (a), (b), and (c) were prepared as above by deficiency diazotisation and removal of unreacted *p*-aminomonomethylaniline; (a) and (b) were given Sandmeyer treatment to obtain the steam-volatile *p*-chloro- and *p*-bromo-monomethylanilines respectively; (c) was acidified with the necessary amount of sulphuric acid and the solution treated with aqueous potassium iodide, whereupon crude *p*-iodomonomethylaniline was precipitated, but as it proved difficult to crystallise owing to the separation of iodine, it was converted by nitrous acid into p-*iodo*-N-*nitrosomethylaniline*, which readily crystallised from 50% aqueous pyridine or light petroleum in long, colourless needles, m. p. 112° (Found: N, 10·8; I, 48·3. $C_7H_7ON_2I$ requires N, 10·7; I, 48·4%), and gave the Liebermann nitroso-reaction.

The authors thank Imperial Chemical Industries Ltd., Dyestuffs Division, for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 18th*, 1944.]

---

## 108. *A Method of Nuclear Methylation of Phenolic Substances.*

By (MISS) M. G. BARCLAY, A. BURAWOY, and G. H. THOMSON.

A method of nuclear methylation of phenolic substances is described. *o*- or *p*-Hydroxyaryl alcohols and -hydroxyarylamines form, when heated above 250°, anhydrohydroxyaryl alcohols (I, X = O) or (II, X = O), which, analogously to the anhydro-4-aminoaryl alcohols (X = NR), spontaneously undergo two reactions: (i) Disproportionation with formation of methylated phenols and unidentified oxidised resins serving as a source of hydrogen. (ii) Condensation to substances containing two or more phenolic groups connected by methylene linkages, such as the crystalline dihydroxydiarylmethanes or the complicated high-molecular phenol–formaldehyde resins, which subsequently decompose with the formation mainly of the original phenols. The second reaction is prevented to a varying degree when the heating is carried out in the presence of suitable alkalis. The bearing of these investigations on the structure and formation of phenol–formaldehyde resins is briefly discussed.

IN a preceding paper (this vol., p. 109) a method of nuclear methylation of aromatic amines (in their *p*-positions) was described, *p*-anhydroaminoaryl alcohols being caused to undergo disproportionation by heating above 300°, *e.g.*, by dry distillation. We thought it possible that anhydro-*o*- or -*p*-hydroxyaryl alcohols of the general type (I, X = O) or (II, X = O) would undergo a similar disproportionation to form nuclear-methylated phenols.

(I.) $[X\text{–}C_6H_4\text{—}CH_2]_n$ (with $CH_2\cdot C_6H_4\cdot X$) $\qquad$ $X\cdot C_6H_4\cdot[CH_2\cdot X\cdot C_6H_4]_n\cdot CH_2$ (II.)

(III.) $X\cdot C_6H_4\cdot[CH_2\cdot X\cdot C_6H_4]_n\cdot CH_2 \longrightarrow HX\cdot C_6H_4\cdot[CH_2\cdot X\cdot C_6H_4]_n\cdot CH_3 \longrightarrow X\cdot C_6H_4\cdot[CH_2\cdot X\cdot C_6H_4]_{n-1}\cdot CH_2 + HX\cdot C_6H_4\cdot CH_3$

*o*- and *p*-Hydroxyaryl alcohols, known to be the first reaction products between phenols and formaldehyde in the presence of alkaline catalysts, possess a great tendency in absence or presence of alkalis and acids to form polyphenolic substances containing methylene linkages between the several phenolic groups, such as the crystalline dihydroxydiarylmethanes and the more complicated high-molecular phenol–formaldehyde resins. Conditions had to be found under which anhydrohydroxyaryl alcohols would be formed and in addition would not undergo the further condensation of the phenol–formaldehyde type at the high temperatures (250—500°) required for a reaction similar to that observed in the case of the anhydro-*p*-aminoaryl alcohols.

3 : 5-Bishydroxymethyl-*p*-cresol was chosen for detailed investigation because it can be obtained readily and in high yield by reaction between *p*-cresol and formaldehyde (2 mols.) in presence of an alkaline catalyst (von Auwers, *Ber.*, 1907, **40**, 2531). Preliminary experiments showed that, when heated above 250°, this substance decomposes with the formation of small amounts of *m*-4-xylenol and mesitol, the two theoretically possible methylated phenols, in addition to considerable amounts of *p*-cresol. The heating was carried out as a distillation, although heating under pressure is also possible. In presence of alkalis, the yield of *m*-4-xylenol and mesitol varies considerably, but is generally higher than that obtained without such additions. In order to compare the effect of different alkalis, the amount of mesitol was determined by treatment of the phenolic distillate with formaldehyde and alkali, any *p*-cresol and *m*-4-xylenol forming non-volatile products and so allowing the separation of the unchanged mesitol by steam-distillation. Its weight was determined, and a correction made for the amount dissolved in water. In all cases, 1 mol. (168 g.) of 3 : 5-bishydroxymethyl-*p*-cresol was distilled. The experimental error should not exceed 2—3 g. Some typical results are shown in Table I, where the type and amount of added material, and the approximate weights of distillate and of mesitol are given.

The best results are obtained in presence of mild alkalis, *i.e.*, oxides and hydroxides of the alkaline earths

and magnesium and the borates of the alkali metals, which neutralise the phenols without making the reaction mixture too alkaline.

When 3 : 5-bishydroxymethyl-*p*-cresol is heated alone or in presence of too weakly alkaline substances, only small amounts of mesitol but considerable amounts of *p*-cresol (and *m*-4-xylenol) are obtained, accompanied by much formaldehyde. This is due to the intermediate formation of condensation products consisting of two or more phenolic groups connected by methylene linkages, which substances decompose above 400° to give mainly the original phenols; *e.g.*, 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenylmethane and 4-hydroxy-3 : 5-bis-(6-hydroxy-3-methylbenzyl)toluene (Koebner, *Z. angew. Chem.*, 1933, **46**, 251) decompose under such conditions in presence or absence of alkalis to give *p*-cresol and traces of *m*-4-xylenol and mesitol. Similarly, 4 : 4′-dihydroxy-2 : 2′-dimethyldiphenylmethane (Eberhardt and Welter, *Ber.*, 1894, **27**, 1814) and 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane (Fries and Hübner, *Ber.*, 1906, **39**, 440) form almost exclusively *o*-cresol and 2-naphthol, only traces of mesitol and 1-methyl-2-naphthol, respectively, being detected. Distillation of the so-called phenol–formaldehyde resins derived from phenol, *o*-, *m*-, or *p*-cresol, or *m*-5-xylenol also yields, as already found in absence of alkalis (Megson, *Trans. Faraday Soc.*, 1935, **32**, 336), mainly the original phenols, and, even in presence of alkalis, only traces of methylated phenols.

The analogous behaviour of 3 : 5-bishydroxymethyl-*p*-cresol and *p*-aminoaryl alcohols is apparent. Both form anhydrides which at high temperatures undergo disproportionation (with the probable intermediate formation of radicals) (III) to afford methylated phenols and amines, respectively, and oxidised resins serving as a source of hydrogen. Both condense to a varying degree (controlled by the presence of alkalis) to form high-molecular substances containing methylene linkages, which spontaneously decompose to form mainly the original amines or phenols.

TABLE I.

| | Added substance, g. | | Distillate, g. | Mesitol, g. |
|---|---|---|---|---|
| (i) | — | | 60 | 3·5 |
| (ii) | ZnO | 122 | 49 | 5 |
| (iii) | $Al_2O_3$ | 51 | 50 | 5 |
| (iv) | $CaCO_3$ | 150 | 53 | 5 |
| (v) | $CaCO_3$ | 150 | 75 | 30 |
| | $Ca(OH)_2$ | 111 | | |
| (vi) | $MgCO_3$ | 126 | 47 | 6 |
| (vii) | $BaCO_3$ | 296 | 50 | 4 |
| (viii) | $BaCO_3$ | 197 | 32 | 16 |
| | $Ca(OH)_2$ | 168 | | |
| (ix) | $Na_2CO_3$ | 159 | 54 | 4 |
| (x) | ,, | 530 | 46 | 4 |
| (xi) | $Na_2CO_3$ | 159 | 78 | 20 |
| | $Na_2B_4O_7$ | 302 | | |
| (xii) | NaOH | 40 | 15 | 3 |
| (xiii) | ,, | 120 | 2 | 1 |
| (xiv) | $Na_2SO_3$ | 189 | 15 | 6 |
| (xv) | $Na_2SO_3$ | 189 | 60 | 22 |
| | $Ca(OH)_2$ | 168 | | |
| (xvi) | $Na_2B_4O_7$ | 168 | 79 | 9 |
| (xvii) | ,, | 302 | 75 | 19 |
| (xviii) | $Na_2B_4O_7$ | 302 | 63 | 22 |
| | $Ca(OH)_2$ | 111 | | |
| (xix) | $CaSO_3$ | 180 | 22 | 3 |
| (xx) | $CaSO_3$ | 180 | 60 | 22 |
| | $Ca(OH)_2$ | 168 | | |
| (xxi) | CaO | 84 | 57 | 20 |
| (xxii) | $Ca(OH)_2$ | 111 | 64 | 32 |
| (xxiii) | ,, | 168 | 77 | 27 |
| (xxiv) | MgO | 60 | 64 | 29 |
| (xxv) | $Mg(OH)_2$ | 87 | 54 | 14 |
| (xxvi) | $Sr(OH)_2$ | 100 | 46 | 20 |
| (xxvii) | $Ba(OH)_2$ | 90 | 67 | 6 |
| (xxviii) | ,, | 257 | 40 | 15 |
| (xxix) | ,, | 514 | 19 | 14 |
| (xxx) | $Ba(OH)_2$ | 257 | 13 | 11 |
| | $Ca(OH)_2$ | 168 | | |
| (xxxi) | Na salt | | 45 | 14 |
| (xxxii) | Na salt | | 51 | 15 |
| | $Ca(OH)_2$ | 168 | | |
| (xxxiii) | Na salt | | 10 | 3 |
| | NaOH | 40 | | |
| (xxxiv) | Na salt | | 2 | 1 |
| | NaOH. | 120 | | |
| (xxxv) | Mg salt | | 60 | 25 |
| (xxxvi) | Ca salt | | 63 | 24 |
| (xxxvii) | Sr salt | | 55 | 28 |
| (xxxviii) | Ba salt | | 57 | 20 |

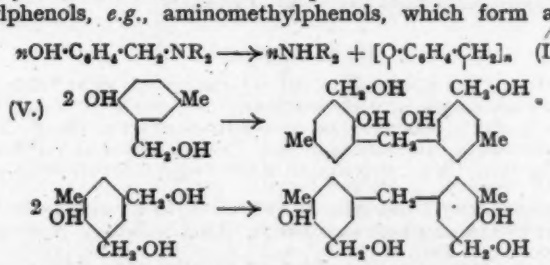
The formation of mesitol from 3 : 5-bishydroxymethyl-*p*-cresol involves the introduction of two methyl groups. The reaction should take place in two stages: (i) Formation and decomposition (disproportionation) of the anhydro-compounds, giving 2 : 4-dimethyl-6-(hydroxymethyl)phenol. (ii) Formation and decomposition of anhydro-2 : 4-dimethyl-6-(hydroxymethyl)phenol, giving mesitol.

Some examples are given to show that the foregoing reaction is characteristic of all hydroxymethylphenols and other substances able to form anhydrohydroxymethylphenols at high temperatures.

Distillation of 3-hydroxymethyl-*p*-cresol (Manasse, *Ber.*, 1894, **27**, 2411) in presence of calcium hydroxide gives a good yield of *m*-4-xylenol in addition to some *p*-cresol and mesitol. As an example of substances other than hydroxymethylphenols, *e.g.*, aminomethylphenols, which form anhydrohydroxymethylphenols

$$n\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NR}_2 \longrightarrow n\text{NHR}_2 + [\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2]_n \quad \text{(IV.)}$$

(V.)




(VI.)

(IV) at high temperatures, 3-piperidinomethyl-*p*-cresol (von Auwers and Dombrowski, *Annalen*, 1906, **344**, 285) behaves similarly. The formation of small amounts of mesitol is doubtless due to condensation of

3-hydroxymethyl- or 3-piperidinomethyl-*p*-cresol, *e.g.*, according to (V), and subsequent decomposition of the condensation product.

3 : 5-Dihydroxymethyl-*o*-cresol [obtained according to Granger, *Ind. Eng. Chem.*, 1932, **24**, 444, from *o*-cresol (1 mol.), formaldehyde (2 mols.), and sodium hydroxide (1 mol.)] yields in presence of calcium hydroxide a mixture of 2 : 4- and 2 : 6-dimethylphenol and mesitol, the xylenols being identified and isolated as the 6- and the 4-nitro-compound, respectively. The yield of mesitol is much smaller than that obtained from 3 : 5-bishydroxymethyl-*p*-cresol owing to the great tendency of the *o*-cresol isomer to condense and form 4 : 4′-dihydroxy-3 : 3′-dimethyl-5 : 5′-bishydroxymethyldiphenylmethane (VI). This substance was obtained by Granger (*loc. cit.*) in small quantity. It is almost exclusively formed when the condensation between *o*-cresol and formaldehyde is carried out in presence of more than 1 mol. of sodium hydroxide and allowed to proceed for many days. Its structure has been established by its preparation from 4 : 4′-dihydroxy-3 : 3′-dimethydiphenylmethane and formaldehyde in presence of alkali. When distilled alone, it yields a mixture of *o*-cresol and *m*-4- and *m*-2-xylenol in addition to traces of mesitol, but in presence of calcium hydroxide a good yield of the two xylenols and mesitol is obtained with only a little *o*-cresol. On distillation, it combines the features of both a hydroxymethylphenol and a dihydroxydiarylmethane.

Distillation of 2-piperidinomethyl-3 : 5-dimethylphenol (von Auwers and Dombrowski, *loc. cit.*) in presence of calcium hydroxide yields mainly *m*-5-xylenol, 2 : 3 : 5-trimethylphenol, and a small amount of 2 : 3 : 5 : 6-tetramethylphenol. 2 : 6-Bishydroxymethyl-3 : 5-dimethylphenol (von Auwers, *loc. cit.*) decomposes in presence of calcium hydroxide to form mainly 2 : 3 : 5-trimethyl- and 2 : 3 : 5 : 6-tetramethyl-phenol. The latter does not react with formaldehyde in presence of an alkaline catalyst. No trace of 3 : 4 : 5-trimethyl-, 2 : 3 : 4 : 5-tetramethyl-, or 2 : 3 : 4 : 5 : 6-pentamethyl-phenol could be found in these experiments, indicating that the above substances are not, as suggested by von Auwers (*loc. cit.*), para-substituted derivatives of *m*-5-xylenol (cf. also Caldwell and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 2354).

Distillation of 1-piperidinomethyl-2-naphthol (von Auwers and Dombrowski, *loc. cit.*) gives in good yield a mixture of β-naphthol and 1-methyl-2-naphthol. The yield of the latter is higher in presence of calcium carbonate, whereas, in contrast to the findings in the case of the benzene derivatives, calcium hydroxide decreases both the total amount of distilled naphthols and that of 1-methyl-2-naphthol. Small amounts of 1-methylnaphthalene have also been observed in these experiments.

The isolation and purification of the hydroxymethyl- or aminomethyl-phenols, being generally difficult and almost always accompanied by considerable loss of material, is unnecessary. The phenols can be condensed with formaldehyde according to known methods, water and unchanged phenol removed by distillation at low temperatures, and the remaining hydroxymethyl- or aminomethyl-phenols heated to the required high temperatures. The catalyst required for the condensation may be chosen from the group of alkalis which give the best yields of methylated phenols in the subsequent heating; generally, calcium hydroxide can be used. In the case of aminomethylphenols, the amine splitting off during the heating can serve as the alkaline medium, but is better supplemented by addition (before distillation) of a suitable alkali such as calcium hydroxide.

This modification permits one to start from a mixture of phenolic substances forming a mixture of hydroxymethyl- or aminomethyl-phenols : it is especially advantageous if an exhaustive methylation of the phenols is desired. For instance, *p*-cresol is condensed with formaldehyde in presence of calcium hydroxide, and the reaction mixture is distilled, the distillate, consisting of *m*-4-xylenol, *p*-cresol, and mesitol, being again condensed with formaldehyde in presence of calcium hydroxide. The reaction mixture, consisting of the hydroxymethyl derivatives of *m*-4-xylenol and *p*-cresol and of unchanged mesitol, is distilled, mesitol being obtained in 30% yield. Similarly, a good yield of mesitol can be obtained from *o*-cresol and phenol, a 20% yield of 2 : 3 : 4 : 6-tetramethylphenol from *m*-cresol, and a 30% yield of 2 : 3 : 5 : 6-tetramethylphenol from *m*-5-xylenol. A mixture of mesitol and 2 : 3 : 4 : 6-tetramethylphenol is also obtained from the very cheap cresylic acids.

The above investigation throws new light on the nature and formation of phenol–formaldehyde resins. (i) It confirms the generally accepted view that these possess structures involving numerous phenolic groups connected by methylene linkages, since, like the crystalline dihydroxydiarylmethanes, they decompose at high temperatures with formation mainly of the original phenols and only traces of methylated phenols. (ii) It shows that their formation can be preceded not only by that of hydroxymethylphenols, but also that of anhydrohydroxymethylphenols, which are stable under certain conditions and, in contrast to the phenol–formaldehyde resins, decompose at high temperatures to form methylated phenols.

## Experimental.

3 : 5-*Bishydroxymethyl*-p-*cresol*.—(a) The distillates in the experiments given in Table I were generally fractionated before determination of mesitol. They consist of various amounts of *p*-cresol (b. p. 200°), identified as 3 : 5-dinitro-*p*-cresol (m. p. 84°), *m*-4-xylenol (b. p. 212°), identified as its 5-nitro-derivative (m. p. 72°), and mesitol (b. p. 219°; m. p. 72°), in addition to small amounts of substances of b. p. >300°, traces of volatile hydrocarbons, and in many cases some formaldehyde. The fractions (in g.) obtained in a few selected experiments are given in Table II, m. p.'s being added in parentheses.

(b) 3 : 5-Bishydroxymethyl-*p*-cresol (15 g.) and calcium hydroxide (15 g.) were heated in a sealed tube for 6 hours at 300°; the resulting mixture was steam-distilled, and mesitol (2 g.) collected. A similar result was obtained when heating was carried out in an autoclave at 300°.

(c) 3 : 5-Bishydroxymethyl-*p*-cresol (100 g.) was heated for 7 hours at 200°, 6 hours at 255°, and 14 hours at 360°, formaldehyde and water distilling over (15·4, 15·8, 19·7 g. respectively). The final distillate consisted of 5·8 g. of formaldehyde and 13·9 g. of water.

TABLE II.

| Experiment. | (i). | (iv). | (ix). | (x). | (xi). | Experiment. | (xvi). | (xvii). | (xxiii). | (xxvii). | (xxviii). |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Distillate * | 60 | 53 | 54 | 46 | 78 | Distillate | 79 | 75 | 77 | 67 | 40 |
| 195—200° | 13 | 7 | 9 | 8 | — | 195—200° | 6 | — | 7 | 9 | 6 |
| 200—205 | 13 | 5 | 13 | 4 | 7 | 200—205 | 1 | 8 | 8 (6°) | 4 (4°) | 6 (20°) |
| 205—210 | 12 | 15 | 8 | 17 | 20 (23°) | 205—210 | 10 (20°) | 13 (22°) | 11 (31°) | 18 (21°) | 14 (25°) |
| 210—215 | 4 (19°) | 5 (12°) | 3 (12°) | 5 (13°) | 31 (36°) | 210—215 | 35 (37°) | 29 (31°) | 26 (46°) | 12 (32°) | 4 (31°) |
| 215—230 | 4 | 6 (17°) | 3 (17°) | 3 (17°) | 7 (45°) | 215—230 | 12 (47°) | 12 (33°) | 11 (54°) | 6 (41°) | 3 (34°) |
| Residue | 5 | 10 | 13 | 7 | 12 | Residue | 10 | 12 | 10 | 12 | 7 |
| Mesitol | 3·5 | 5 | 4 | 4 | 20 | Mesitol | 9 | 19 | 27 | 6 | 15 |

* The distillates were in all cases slightly wet.

3-*Hydroxymethyl*-p-*cresol*.—This substance (138 g.) and calcium hydroxide (138 g.) were distilled; yield, 57 g. Fractions (mainly *m*-4-xylenol, little *p*-cresol and mesitol); 200—205°, 8 g.; 205—210°, 15 g.; 210—220°, 17 g.; high-boiling residue, 8 g.

3-*Piperidinomethyl*-p-*cresol*.—This substance (206 g.) and calcium hydroxide (206 g.) were distilled. After removal of piperidine, the residual oil (58 g.) was fractionated. Fractions (mainly *m*-4-xylenol, some *p*-cresol and mesitol): 200—205°, 13 g.; 205—210°, 13 g.; 210—220°, 22 g.; high-boiling residue, 9 g.

2 : 2′-*Dihydroxy*-5 : 5′-*dimethyldiphenylmethane* (loc. cit.).—(*a*) This substance (50 g.) and sodium carbonate (50 g.) were distilled; yield, 32 g. Fractions: 195—200°, 27 g. (almost pure *p*-cresol); residue, 3 g. (*b*) This phenol (50 g.) and calcium hydroxide (50 g.) were distilled; yield, 20 g. Fractions (mainly *p*-cresol, traces of *m*-4-xylenol and mesitol): 190—200°, 5 g.; 200—205°, 10 g.; residue, 5 g.

4-*Hydroxy*-3 : 5-*bis*-(6-*hydroxy*-3-*methylbenzyl*)*toluene* (loc. cit.).—This substance (100 g.) was distilled alone and in presence of sodium carbonate (100 g.) or calcium hydroxide (100 g.); yield, about 60 g. Low-boiling fractions (36—44 g.) consist mainly of *p*-cresol, with traces of *m*-4-xylenol and mesitol.

4 : 4′-*Dihydroxy*-5 : 5′-*dimethyldiphenylmethane* (loc. cit.).—This substance (50 g.) was distilled in presence of sodium carbonate (50 g.) or calcium hydroxide (50 g.); yield, 36—38 g. of oil, mostly boiling at 183—193° (mainly *o*-cresol). Neither *m*-4- nor *m*-2-xylenol could be detected, but traces of mesitol were present. When refluxed alone for 14 hours, the substance decomposes with a similar result.

4 : 4′-*Dihydroxy*-3 : 3′-*dihydroxymethyl*-5 : 5′-*dimethyldiphenylmethane*.—*Preparation*. *o*-Cresol (108 g.) and sodium hydroxide (50 g.) were dissolved in water (200 c.c.), and 40% formaldehyde (160 c.c.) added. After a week, the product was precipitated by means of carbon dioxide; needles, m. p. 163°, from alcohol (Found: C, 70·3; H, 6·7. Calc. for $C_{17}H_{20}O_4$: C, 70·8; H, 6·9%). It is also obtained by treatment of 4 : 4′-dihydroxy-5 : 5′-dimethyldiphenylmethane with formaldehyde and sodium hydroxide.

*Distillation*. This substance (150 g.) was distilled alone and in presence of calcium hydroxide (respective results are separated by an oblique stroke); distillate, 50/50 g. Fractions: 190—195°, 7/8 g.; 195—200°, 17/7 g.; 200—205°, 10/12 g. (m. p. 10°); 205—210°, 4 g. (m. p. 7°)/8 g. (m. p. 17°); 210—230°, 3 g. (m. p. 16°)/8 g. (m. p. 27°); high-boiling residue, 7/5 g.; mesitol, 3/8 g. (*m*-2-Xylenol, b. p. 202°, m. p. 47°, was identified as its 5-nitro-derivative, m. p. 170°.)

3 : 5-*Bishydroxymethyl*-o-*cresol*.—*Preparation*. *o*-Cresol, sodium hydroxide, and formaldehyde were condensed exactly as in the preceding preparation. After two days, acetic acid (60 g.) was added, whereupon 3 : 5-bishydroxymethyl-*o*-cresol slowly separated; m. p. 94°, after crystallisation from chloroform or, better, nitrobenzene.

*Distillation*. The substance (168 g.) was distilled in presence of calcium hydroxide (168 g.); distillate, 48 g. Fractions: <190, 10 g.; 190—200°, 9 g. (m. p. 16°); 200—205°, 9 g. (m. p. 26°); 205—210°, 9 g. (m. p. 32°); residue, 9 g.; mesitol, 12 g.

2-*Piperidinomethyl*-3 : 5-*dimethylphenol* (von Auwers and Dombrowski, *loc. cit.*).—This substance (219 g.) was distilled in presence of calcium hydroxide (219 g.). After removal of piperidine, the distillate (68 g.) was fractionated. Fractions [containing mainly *m*-5-xylenol (b. p. 220°; m. p. 64°), 2 : 3 : 5-trimethylphenol (b. p. 230°; m. p. 95°), and some 2 : 3 : 5 : 6-tetramethylphenol (b. p. 249°; m. p. 117°)]: 215—220°, 5 g.; 220—225°, 12 g. (m. p. 42°); 225—230°, 19 g. (m. p. 55°); 230—235°, 8 g. (m. p. 56°); 235—240°, 8 g. (m. p. 57°); residue, 10 g.; 2 : 3 : 5 : 6-tetramethylphenol, 4 g.

2 : 6-*Bishydroxymethyl*-3 : 5-*dimethylphenol* (von Auwers, *loc. cit.*).—This substance (183 g.) and calcium hydroxide (183 g.) were distilled; distillate, 78 g. Fractions: <225°, 9 g.; 225—230°, 6 g. (m. p. 55°); 230—235°, 12 g. (m. p. 66°); 235—240°, 8 g. (m. p. 74°); 240—250°, 8 g. (m. p. 75°); residue, 15 g.; 2 : 3 : 5 : 6-tetramethylphenol, 24 g.

1-*Piperidinomethyl*-2-*naphthol* (von Auwers and Dombrowski, *loc. cit.*).—(*a*) The substance (250 g.) was distilled. After removal of piperidine, the distillate (110 g.) was treated with formaldehyde and alkali, whereupon the β-naphthol present formed 2 : 2′-dihydroxy-1 : 1′-dinaphthylmethane. Steam-distillation under alkaline conditions afforded a small amount of oil, mainly 1-methylnaphthalene, identified by its picrate (m. p. 141°); the residue was acidified, and 1-methyl-2-naphthol extracted with boiling water; yield, 22 g. (*b*) Distillation was carried out in presence of calcium carbonate (250 g.), sodium carbonate (250 g.), and calcium hydroxide (250 g.). Distillate, 118/52/57 g.; 1-methyl-2-naphthol, 30/10/13 g.

2 : 2′-*Dihydroxy*-1 : 1′-*dinaphthylmethane*.—When this was distilled alone or in presence of sodium carbonate or calcium hydroxide, considerable amounts of β-naphthol, in addition to traces of 1-methylnaphthalene and 1-methyl-2-naphthol (in all cases less than 2%), were formed.

| | *o*-Cresol. | | *p*-Cresol. | | Phenol. | | |
|---|---|---|---|---|---|---|---|
| No. of distns. | 1. | 2. | 1. | 2. | 1. | 2. | 3. |
| Distillate | 66 | 48 | 68 | 62 | 40 | 34 | 30 |
| <200° | 7 | — | — | — | 10 | — | — |
| 200—205 | 9 | — | — | — | 3 | 3 | 1 |
| 205—210 | 12 | 2 | 7 | — | 6 | 4 (10°) | 1 (22°) |
| 210—215 | 9 | 7 (40°) | 9 (35°) | 3 | 10 (20°) | 4 (28°) | 2 (38°) |
| 215—220 | 8 (45°) | 14 (56°) | 20 (46°) | — | — | 6 (45°) | 4 (49°) |
| 220—230 | 4 (55°) | 11 (65°) | 17 (58°) | 42 (63°) | — | 5 (55°) | 9 (59°) |
| Residue | 8 | 5 | 10 | 8 | 3 | 6 | 5 |
| Mesitol | 14 | 20 | 26 | 41 | 4 | 11 | 13 |

| | *m*-Cresol. | | | *m*-5-Xylenol. | | Cresylic acids. | |
|---|---|---|---|---|---|---|---|
| No. of distns. | 1. | 2. | 3. | 1. | 2. | 3. | 3. |
| Distillate | 58 | 47 | 47 | 75 | 68 | 44 | 40 |
| <215° | 8 | — | — | — | — | — | — |
| 215—220 | 11 | — | — | — | — | 6 (60°) * | 2 (44°) * |
| 220—225 | 11 (9°) | 7 | — | 3 (51°) | — | 14 (68°) | 2 (52°) |
| 225—230 | 7 (9°) | 6 (19°) | 4 | 3 (51°) | 3 (58°) | 3 (59°) | 5 (56°) |
| 230—235 | 4 (14°) | 4 (24°) | 4 (30°) | 7 (57°) | 4 (64°) | 2 (49°) | 4 (48°) |
| 235—240 | 3 (19°) | 7 (32°) | 7 (39°) | 19 (67°) | 8 (78°) | 4 (40°) | 2 (40°) |
| 240—250 | 4 (23°) | 4 (40°) | 16 (51°) | 15 (84°) | 28 (98°) | — | 6 (58°) |
| 250—260 | — | 4 (55°) | 3 (56°) | 10 (86°) | 9 (87°) | — | — |
| 260—280 | — | — | 3 (45°) | — | 5 (83°) | — | — |
| Residue | 7 | 8 | 5 | 9 | 6 | — | — |
| Mesitol | — | — | — | — | — | 32 † | 23 † |
| 2 : 3 : 4 : 6-Tetramethylphenol | 5 | 14 | 29 | — | — | | |
| 2 : 3 : 5 : 6-Tetramethylphenol | — | — | — | 28 | 46 | — | — |

* Fractions of the mixture of mesitol and 2 : 3 : 4 : 6-tetramethylphenol obtained by steam distillation in presence of alkali and formaldehyde.

† Total amounts of mixtures of mesitol and 2 : 3 : 4 : 6-tetramethylphenol.

*Exhaustive Distillation.*—The phenol (1 mol.), an equal quantity of calcium hydroxide, and 40% formaldehyde (3 mols.; but in the case of phenol, *m*-cresol, and the cresylic acids, 4 mols.) were mixed, with cooling; after standing overnight, the reaction mixture containing the poly(hydroxymethyl)phenols was distilled. The distillate was again treated with an equal weight of calcium hydroxide and 100 c. c. of 40% formaldehyde solution, and the reaction mixture distilled. With phenol, *m*-cresol, and the cresylic acids the process was repeated a third time, 50 c.c. of a 40% formaldehyde solution being used. The distillates were fractionated, and the amount of mesitol (m. p. 72°), 2 : 3 : 4 : 6-tetramethylphenol (m. p. 80°), or 2 : 3 : 5 : 6-tetramethylphenol (m. p. 117°) was determined by treatment of the distillates with formaldehyde and alkali and steam distillation, the volatile unchanged phenols being collected. The results are tabulated above, weights being in g.

The authors thank the Calico Printers' Association, Ltd., Manchester, for permission to publish this paper.

College of Technology, Manchester 1. [*Received, January 19th*, 1944.]

---

## 109. *Steric Inhibition of Resonance. Part I. The Dichloronitrobenzenes.*

By George Thomson.

The molecular solution volumes and molecular refractivities of the six isomeric dichloronitrobenzenes are interpreted as supporting the view that in 2 : 6-dichloronitrobenzene resonance between the nitro-group and the benzene nucleus is to a large extent inhibited and that even one chlorine ortho to a nitro-group will have a certain inhibitory effect on the resonance. Variations in the parachors are of the same magnitude and sign as the variations in molecular solution volumes.

Values found for their dipole moments are not inconsistent with this view.

The abnormally low reactivity of the chlorine atoms in 2 : 6-dichloronitrobenzene noted by Holleman and de Mooy (*Rec. Trav. chim.*, 1915, **35**, 19) has been discussed by Hückel ("Theoretische Grundlagen der organischen Chemie," 1931, ii, 256, 272; *Ber.*, 1929, **62**, 2041), who has calculated the energy of activation from Holleman's measurements. More recently, Loudon and Shulman (J., 1941, 725) have suggested that the low reactivity results from inhibition by the chlorine atoms of the resonance between the nitro-group and the benzene nucleus. Such steric inhibition of resonance was first postulated by Hampson and his collaborators (J., 1937, 10; 1939, 981) to account for the unexpectedly low dipole moments of nitro- and dimethylamino-durene derivatives. Hammick and Hellicar (J., 1938, 761), discussing the steric effects of chlorine and methyl substituents, point out that, the radius of the chlorine atom being taken as 0·99 A., and the radius of revolution of C–H in methyl as 1·09 A., a scale diagram shows that the surface of the chlorine atom will be 0·07 A. nearer than the sphere of revolution of the methyl group to an atom or group on the benzene nucleus between them. The chlorine atom would therefore be expected to be just as effective as the methyl group in inhibiting resonance.

If in 2 : 6-dichloronitrobenzene the vicinal chlorine atoms inhibit resonance between the nitro-group and the benzene nucleus, certain physical properties may be expected to differentiate this compound from its isomers.

Since the oxygen atoms of the nitro-group will be forced out of the plane of the benzene ring, the carbon–nitrogen bond will revert from partial double-bond to single-bond character with consequent lengthening: the molecules will be less easily packed and one would expect the molecular volume to be greater than that of an isomer such as 3 : 4- or 3 : 5-dichloronitrobenzene in which resonance is likely to be quite uninhibited. Such a volume change may be reflected in the parachor.

Further, inhibition of the resonance between the nitro-group and the benzene ring would be expected to result in a lowering of the molecular refractivity. It is known that the atomic refractivity of the nitro-group is lower in nitroparaffins than in nitrobenzenes, and the relevant structural difference appears to be the occurrence in the latter of resonance between the nitro-group and the benzene nucleus. Brühl (*Z. physikal. Chem.*, 1898, **25**, 613) gives the atomic refractivity (for the D line) of the nitro-group in nitrobenzenes as 7·30 and in

nitroparaffins as 6·72, a difference of 0·58 unit. If Eisenlohr's recalculated values of atomic refractivity are used a rather larger difference is found: his value (*ibid.*, 1912, **79**, 129) for the nitro-group in nitroparaffins containing up to five carbon atoms is 6·638, and in those containing 6—10 carbon atoms 6·582. On the same basis the value for the nitro-group in nitrobenzene is calculated as 7·53, giving a difference between the aliphatic and the aromatic nitro-group of 0·95.

Finally, the dipole moment of 2 : 6-dichloronitrobenzene would be expected, like that of nitrodurene, to be lower than the value calculated by vectorial addition of the constituent moments after allowance for induction effects.

In order to test these points, measurements of molecular solution volume, molecular refractivity, and dipole moment have been made in benzene solution at 25°, and the parachors have been calculated from measurements of density and surface tension made on liquid dichloronitrobenzenes at 100°. All six isomers have been investigated.

*Discussion of Results.*—In Table I are collected the values of molecular solution volumes (M.S.V.), parachor, and molecular refractivity for sodium yellow ($\lambda = 5893$ A.) and mercury green ($\lambda = 5461$ A.). Measurements were made on solutions in which the concentration of dichloronitrobenzene varied between about 4 and

TABLE I.

*Data for dichloronitrobenzenes.*

| Isomer. | M.S.V. | [*P*]. | $[R_L]_D$. | $[R_L]_{5461}$. | *Q*. | Isomer. | M.S.V. | [*P*]. | $[R_L]_D$. | $[R_L]_{5461}$. | *Q*. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 : 4- | 125·7 | 333·4 | 43·00 | 43·15 | 22·3 | 2 : 4- | 126·7 | 335·7 | 42·62 | 42·84 | 22·7 |
| 3 : 5- | 125·6 | 334·5 | 42·94 | 43·19 | — | 2 : 5- | 126·7 | 336·2 | 42·50 | 42·72 | 23·2 |
| 2 : 3- | 126·4 | 335·8 | 42·63 | 42·79 | 23·0 | 2 : 6- | 130·4 | 340·1 | 42·32 | 42·46 | 25 |

6 mols. %. The last col. contains the values of energy of activation (for the reaction with sodium methoxide) calculated by Hückel (*loc. cit.*).

It will be seen that the values fall into three well-defined groups, depending on the extent to which the ortho-positions to the nitro-group are substituted by chlorine, the regularities in molecular refractivity being better defined in the values for mercury green. The lowest values of molecular solution volume and parachor and the highest values of molecular refractivity are those of 3 : 5- and 3 : 4-dichloronitrobenzenes: the values for these two isomers are identical within the limits of experimental error. When one chlorine occupies a position ortho to the nitro-group, both the molecular solution volume and the parachor are slightly raised and the molecular refractivity is lowered: the values for 2 : 3-, 2 : 4-, and 2 : 5-dichloronitrobenzenes are indistinguishable from one another but differ from those for 3 : 4- and 3 : 5-dichloronitrobenzenes by more than the experimental error. In the 2 : 6-isomer there is a further considerable increase in molecular solution volume and in parachor and a decrease in molecular refractivity approximately the same as that occasioned by the presence of one chlorine as an ortho-substituent. Much the same grouping of the isomers is possible on the basis of Hückel's values for their energies of activation. The difference in molecular refractivity for sodium yellow between 3 : 5- and 2 : 6-dichloronitrobenzene is 0·62, indicating that in the latter compound the atomic refractivity of the nitro-group is closer to the value for the group in a nitroparaffin than to the value in nitrobenzene. Values collected in Table II, where Δ is the difference due to one nitro-group, show that a reduction in molecular refractivity is observed whenever the 2 : 6 positions in nitrobenzene are substituted by methyl, chlorine, or bromine. The effect is most easily demonstrated by comparing the differences between the nitro- and the corresponding unnitrated compounds.

TABLE II.

| Compound. | $[R_L]_D$. | Δ. | $[R_L]_{5461}$. | Δ. |
|---|---|---|---|---|
| Benzene | 26·18 [1] | 6·56 | 26·36 [2] | 6·68 |
| Nitrobenzene | 32·74 [1] | | 33·04 [2] | |
| Mesitylene | 40·76 | 6·22 | 41·06 | 6·16 |
| Nitromesitylene | 46·98 | | 47·22 | |
| *s*-Trichlorobenzene | 40·9 [3] | 6·2 | — | — |
| 1 : 3 : 5-Trichloro-2 : 4 : 6-trinitrobenzene | 59·5 [3] | | — | — |
| *s*-Tribromobenzene | 49·9 [3] | 6·07 | — | — |
| 1 : 3 : 5-Tribromo-2 : 4 : 6-trinitrobenzene | 68·1 [3] | | — | — |
| *m*-Dichlorobenzene | 36·16 | 6·78 | 36·40 | 6·79 |
| 3 : 5-Dichloronitrobenzene | 42·94 | | 43·19 | |
| *m*-Dichlorobenzene | 36·16 | 6·16 | 36·40 | 6·06 |
| 2 : 6-Dichloronitrobenzene | 42·32 | | 42·46 | |
| Chloroform | 21·40 [1] | 5·92 | 21·49 [2] | 5·94 |
| Chloropicrin | 27·32 [1] | | 27·43 [2] | |

[1] Landolt-Börnstein "Tabellen." [2] *Ibid.*, by interpolation. [3] Tiganik, *Z. physikal. Chem.*, 1931, *B*, **13**, 425.

It might be objected that, in the aromatic compounds instanced, possibly not the nitro-group but one or both of the other groups is suffering distortion. This seems unlikely, since trichlorination of mesitylene results in the same increase of molecular refractivity as trichlorination of benzene to give *s*-trichlorobenzene. Admittedly, the differences in molecular refractivity in the dichloronitrobenzene series are small but they appear to be real, and if it is granted that the reduction in the atomic refractivity of the nitro-group occasioned by two bulky ortho-substituents is due to inhibition of resonance, it is difficult to avoid the conclusion that

even one such ortho-substituent can have some inhibitory effect on the resonance between the nitro-group and the benzene nucleus. Baddeley (*Nature*, 1939, **144**, 444) has explained some "ortho" phenomena due to a single ortho-substituent on the basis of inhibited resonance, and Loudon and Shulman (*loc. cit.*) also refer to this possibility.

Interpretation of the dipole moments of the dichloronitrobenzenes is complicated by the necessity for a knowledge of the magnitude of the inductive effects between the substituents. Exact calculation of these effects is impossible in view of the uncertainty of the locus of the resultant moment of the nitro-group: small changes in its location produce large changes in the induced moments in groups in its immediate neighbourhood, and it seems probable that in considering inductive interaction between ortho-substituents and a nitro-group it would be necessary to analyse the nitro-group into its component dipoles and consider the induction due to each separately. Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919), who first attempted to calculate the induction effects in disubstituted benzene derivatives, invariably found discrepancies when a nitro-group was one of the substituents, and Brown, de Bruyne, and Gross (*ibid.*, 1934, **56**, 1291), who applied Smallwood and Herzfeld's treatment to mesitylene derivatives, failed to get agreement between their experimental and calculated moments for nitromesitylene, though in this case the discrepancy could no doubt be explained in part by inhibition of resonance due to the vicinal methyl groups. In Hampson's approximate calculations of the induced moments in nitrodurene, it was possible on account of the low moment of the $H_3C$–C link to neglect its inductive effect on the nitro-group. This is not possible with the Cl–C link, and so resort has been made to empirical methods in order to obtain the "calculated" values of moment of the dichloronitrobenzenes set out in Table IV. (All values of dipole moments in this paper are in Debye units.) The A series of values are obtained by compounding the moments of nitrobenzene and the appropriate dichlorobenzene: in this way some correction is made for the interaction of the two chlorine atoms. The B series embody a further correction for the interaction of the chlorine atoms and the nitro-group estimated from the deviations of the observed moments of the chloronitrobenzenes from the values calculated by vector addition. Tiganik's values (*loc. cit.*) for the chloronitrobenzenes have been used in preference to Lutgert's (*Z. physikal. Chem.*, 1931, *B*, **14**, 350), which seem improbably low in comparison with the values found in the vapour phase by Groves and Sugden (J., 1937, 1782) and, moreover, are open to the objection that they were determined by the temperature–solution method.

TABLE III.

*Dipole moments of the chloronitrobenzenes.*

| | Tiganik. | | Groves and Sugden. | | Lutgert. |
|---|---|---|---|---|---|
| | Obs. | Calc. | Obs. | Calc. | Obs. |
| *o*-$C_6H_4Cl\cdot NO_2$ | 4·33 | 4·92 | 4·59 | 5·32 | 3·96 |
| *m*-$C_6H_4Cl\cdot NO_2$ | 3·40 | 3·46 | 3·69 | 3·69 | 3·12 |
| *p*-$C_6H_4Cl\cdot NO_2$ | 2·57 | 2·42 | 2·78 | 2·51 | 2·34 |

Since Tiganik's values for the chloronitrobenzenes are to be used, it has been thought desirable to use also his values (*loc. cit.*) for nitrobenzene and the dichlorobenzenes, *viz.*, $C_6H_5\cdot NO_2$, 3·97; *o*-$C_6H_4Cl_2$, 2·25; *m*-$C_6H_4Cl_2$, 1·48; *p*-$C_6H_4Cl_2$, 0. The following assumptions are made regarding interaction of chlorine and nitro-groups. (*a*) Each chlorine ortho to a nitro-group will result in a diminution of moment of 0·59 D. (the difference between the observed and calculated values for *o*-chloronitrobenzene in benzene solution). This correction includes at least two factors, *viz.*, the effect of induction and the effect of inhibition of resonance; in the present state of our knowledge it is impossible to assess them separately. (*b*) A chlorine meta to a nitro-group will have no effect (cf. identity of calculated and experimental gas values for *m*-chloronitrobenzene and the closeness of the corresponding solution values). (*c*) A chlorine para to a nitro-group will result in an increase of moment to 0·15 D. (the difference between observed and calculated values for *p*-chloronitrobenzene).

The experimental and the calculated values of dipole moments of the dichloronitrobenzenes are given in Table IV. In the case of 2 : 5-dichloronitrobenzene, the only isomer whose moment has previously been measured, the value now found is identical with that found by Hassel and Naeshagen (*Z. physikal. Chem.*, 1931, *B*, **12**, 79).

TABLE IV.

*Dipole moments of dichloronitrobenzenes.*

| Isomer. | 2 : 3. | 2 : 4. | 2 : 5. | 2 : 6. | 3 : 4. | 3 : 5. |
|---|---|---|---|---|---|---|
| Found | 3·86 | 2·66 | 3·45 | 4·18 | 2·17 | 2·66 |
| Calc. (A) | 4·56 | 3·47 | 3·97 | 5·45 | 2·31 | 2·49 |
| Calc. (B) | 3·97 | 3·03 | 3·38 | 4·27 | 2·46 | 2·49 |

Despite the empirical nature of the treatment, the calculated results show a fair agreement with the experimental (within 2—7%), with the notable exceptions of the values for 2 : 4- and 3 : 4-dichloronitrobenzenes, *i.e.*, the only two isomers which have a chlorine substituted para to the nitro-group. Now a para-substituted nitrobenzene normally has a value of moment higher than that calculated as the vector sum of the moments. It is unlikely that this exaltation of moment is due to induction; more probably it results from interaction of resonance effects as shown so much more markedly in the familiar case of *p*-nitroaniline. In the case of

2 : 4-dichloronitrobenzene the chlorine ortho to the nitro-group will, if it inhibits the resonance between the nitro-group and the benzene nucleus, in a proportionate degree cause a departure from the character of nitrophenyl so that the second chlorine entering para to the nitro-group will not increase the moment by 0·15. This argument, however, cannot apply in the case of 3 : 4-dichloronitrobenzene, in which the resonance of the nitro-group with the benzene nucleus would be expected to be unimpaired as will that of the para-chlorine.*

The case of 3 : 5-dichloronitrobenzene is rather surprising. It should not be complicated by induction effects or inhibition of resonance, and one would expect a rather closer agreement between the observed and the calculated moment than is shown here.

## Experimental.

*Materials.*—Solvent benzene was purified in the usual manner. Mesitylene had b. p. 163·5°, $d_4^{25°}$ 0·85948, $n_D^{25°}$ 1·49698, whence $[R_L]_D$ 40·76, in good agreement with the value 40·79 ± 0·05 given by Mulliken (*J. Chem. Physics*, 1939, **7**, 356) quoting from Egloff's "Physical Constants of Hydrocarbons"; $n_{5461}^{25°}$ 1·5000, whence $[R_L]_{5461}$ 41·06. *m*-Dichlorobenzene had b. p. 171—171·4°/755 mm., $d_4^{25°}$ 1·2824, $n_D^{25°}$ 1·54400, whence $[R_L]_D$ 36·16, $n_{5461}^{25°}$ 1·54834, whence $[R_L]_{5461}$ 36·40. Nitromesitylene (m. p. 44°) was prepared as in *Organic Syntheses*, **14**, 68.

3 : 4- and 2 : 5-Dichloronitrobenzenes were purchased from B.D.H., distilled under reduced pressure, and recrystallised; m. p.'s 43° and 55°, respectively. 2 : 3-Dichloronitrobenzene (m. p. 61°) was prepared as described by Kremer and Bendich (*J. Amer. Chem. Soc.*, 1939, **61**, 2658). 3 : 5-, 2 : 4-, and 2 : 6-Dichloronitrobenzene (m. p.'s 65°, 33°, and 71°, respectively) were prepared by the methods of Holleman and Reiding (*Rev. Trav. chim.*, 1904, **23**, 357).

*Measurements.*—Refractive indices were measured on a Hilger–Pulfrich refractometer, and dielectric constants by means of the apparatus described in previous papers.

For measurements of surface tension at 100°, Ferguson's method (*Proc. Physical Soc.*, 1932, **44**, 511) was adopted. The horizontal capillary tube (0·0592 cm. bore) was a sliding fit in a brass tube which was steam-jacketed. The manometer liquid was high-boiling (>120°) light petroleum, and the differences in level were measured by means of a cathetometer. To test the apparatus, the surface tension of a purified specimen of *p*-chloronitrobenzene was measured. The values found, 35·33 and 35·27 dynes/cm., are in good agreement with Sugden's value 35·40 (J., 1924, 1167) and, like his, rather higher than that of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 138).

Densities at 100° were measured under comparable conditions. The pyknometer (kindly lent by Dr. James Bell) was made from pyrex tubing of about 1 mm. bore, and fitted into a slot in a plate of brass enclosed in a vessel through which was passed a vigorous stream of steam. Densities of 2 : 4-, 2 : 5-, and 3 : 4-dichloronitrobenzenes have been measured over a range of temperatures by Jaeger (*loc. cit.*), and the values now recorded are in good agreement with those obtained by interpolation from his data.

*Densities, surface tensions, and parachors of dichloronitrobenzenes at* 100°.

[J. = Value due to Jaeger (*loc. cit.*).]

| Compound. | $\gamma^{100°}$ (dynes/cm.) | $d_4^{100°}$. | [*P*]. |
|---|---|---|---|
| 2 : 3-Isomer ..... | 38·26, 38·21, 38·22, 38·20; mean 38·22 | 1·421, 1·421 | 335·8 |
| 2 : 4-Isomer ..... | 37·18, 37·17, 37·32, 37·20; mean 37·22 (J. 34·8) | 1·411, 1·413 (J. 1·416) | 335·7 |
| 2 : 5-Isomer ..... | 37·14, 37·13, 37·15, 37·09, 37·06, 37·06; mean 37·10 (J. 34·9) | 1·409, 1·408 (J. 1·410) | 336·2 |
| 2 : 6-Isomer ..... | 36·21, 36·17, 36·21; mean 36·20 | 1·383, 1·385 | 340·1 |
| 3 : 4-Isomer ..... | 37·43, 37·48, 37·49, 37·44; mean 37·46 (J. 35·2) | 1·422, 1·424 (J. 1·424) | 333·4 |
| 3 : 5-Isomer ..... | 35·55, 35·60, 35·55, 35·50, 35·52, 35·59, 35·66; mean 35·57 | 1·399, 1·402 | 334·5 |

*Refractivity measurements in benzene solution at* 25°.

| Solute. | Mol.-fraction solute. | $d_4^{25°}$. | M.S.V. | $n_D^{25°}$. | $[R_L]_D$. | $n_{5461}^{25°}$. | $[R_L]_{5461}$. |
|---|---|---|---|---|---|---|---|
| (Benzene) ..... | — | 0·87342 | — | 1·49786 | 26·174 | 1·50201 | 26·361 |
| Nitromesitylene ..... | 0·044389 | 0·88797 | — | 1·49956 | 47·04 | 1·50362 | 47·21 |
| | 0·058526 | 0·89251 | — | 1·49998 | 46·92 | 0·50418 | 47·23 |
| 2 : 3-Dichloronitrobenzene | 0·04783 | 0·91623 | 126·4 | 1·50365 | 42·59 | 1·50776 | 42·71 |
| | 0·063181 | 0·92852 | 126·3 | 1·50490 | 42·66 | 1·50911 | 42·88 |
| | 0·046188 | 0·91485 | 126·2 | 1·50356 | 42·65 | 1·50767 | 42·78 |
| 2 : 4-Dichloronitrobenzene | 0·050586 | 0·91847 | 126·7 | 1·50393 | 42·62 | 1·50813 | 42·86 |
| | 0·044671 | 0·91330 | 126·7 | 1·50323 | 42·62 | 1·50738 | 42·82 |
| 2 : 5-Dichloronitrobenzene | 0·057529 | 0·92456 | 126·7 | 1·50454 | 42·52 | 1·50869 | 42·68 |
| | 0·054260 | 0·92163 | 126·8 | 1·50416 | 42·44 | 1·50841 | 42·77 |
| | 0·044683 | 0·91335 | 126·5 | 1·50318 | 42·57 | 1·50724 | 42·70 |
| 2 : 6-Dichloronitrobenzene | 0·050841 | 0·91690 | 130·3 | 1·50242 | 42·29 | 1·50654 | 42·48 |
| | 0·054156 | 0·91963 | 130·4 | 1·50276 | 42·36 | 1·50682 | 42·51 |
| | 0·053725 | 0·91918 | 130·4 | 1·50261 | 42·31 | 1·50659 | 42·38 |
| 3 : 4-Dichloronitrobenzene | 0·052012 | 0·92020 | 125·8 | 1·50477 | 42·93 | 1·50896 | 43·20 |
| | 0·035684 | 0·90585 | 125·5 | 1·50280 | 43·07 | 1·50682 | 43·10 |
| 3 : 5-Dichloronitrobenzene | 0·044626 | 0·91370 | 125·8 | 1·50379 | 42·93 | 1·50799 | 43·16 |
| | 0·054092 | 0·92214 | 125·6 | 1·50509 | 42·93 | 1·50925 | 43·15 |
| | 0·058348 | 0·92587 | 125·7 | 1·50574 | 42·97 | 1·51001 | 43·27 |

In the following tables the symbols have their usual significance. The solvent benzene used had $d_4^{25°}$ 0·87368, $n_D^{25°}$ 1·49818, $\varepsilon_{25°}$ 2·2725. In calculating $P_O$, $P_E$ has been taken as 42·7 (the sum of the atomic refractivities) and $P_A$ as 5% of $P_E$.

* Resonance between a substituent such as chlorine and the benzene ring is unaffected by bulky ortho-substituents; *e.g.*, the moments of chloromesitylene and chlorobenzene are identical, as are the moments of bromomesitylene and bromobenzene, and bromodurene has a moment of 1·55 as compared with 1·52 for bromobenzene.

*Dipole-moment measurements.*

| $f_2$. | $d_4^{25°}$. | $\epsilon_{25°}$. | $P_2$. | $f_2$. | $d_4^{25°}$. | $\epsilon_{25°}$. | $P_2$. |
|---|---|---|---|---|---|---|---|
| 2 : 3-Dichloronitrobenzene. | | | | 2 : 4-Dichloronitrobenzene. | | | |
| 0·0074465 | 0·88032 | 2·4307 | 340·5 | 0·0037364 | 0·87721 | 2·3115 | 190·1 |
| 0·009436 | 0·88206 | 2·4730 | 337·9 | 0·006558 | 0·87960 | 2·3408 | 189·2 |
| 0·010579 | 0·88304 | 2·4980 | 336·7 | 0·0091498 | 0·88212 | 2·3679 | 188·1 |
| 0·012712 | 0·88502 | 2·5433 | 333·5 | 0·012787 | 0·88540 | 2·4051 | 188·9 |
| 0·015363 | 0·88742 | 2·6019 | 332·4 | 0·016389 | 0·88849 | 2·4416 | 184·7 |
| 0·019626 | 0·89118 | 2·6930 | 326·9 | $P_2 = 192·2$; $P_O = 147·4$; $\mu = 2·66$. | | | |
| $P_2 = 352$; $P_O = 308·2$; $\mu = 3·86$. | | | | | | | |
| 2 : 5-Dichloronitrobenzene. | | | | 2 : 6-Dichloronitrobenzene. | | | |
| 0·0049737 | 0·87828 | 2·3559 | 280·2 | 0·0041762 | 0·87744 | 2·3772 | 399·0 |
| 0·006804 | 0·88003 | 2·3837 | 273·2 | 0·0049204 | 0·87808 | 2·3965 | 399·3 |
| 0·008382 | 0·88160 | 2·4070 | 266·3 | 0·0081384 | 0·88088 | 2·4760 | 390·7 |
| 0·0096347 | 0·88252 | 2·4270 | 265·9 | 0·012275 | 0·88448 | 2·5785 | 382·2 |
| 0·012828 | 0·88550 | 2·4728 | 257·6 | 0·015039 | 0·88688 | 2·6475 | 377·6 |
| $P_2 = 291·5$; $P_O = 246·7$; $\mu = 3·45$. | | | | $P_2 = 407$; $P_O = 362·2$; $\mu = 4·18$. | | | |
| 3 : 4-Dichloronitrobenzene. | | | | 3 : 5-Dichloronitrobenzene. | | | |
| 0·004548 | 0·87791 | 2·3050 | 141·1 | 0·0035416 | 0·87693 | 2·3073 | 182·2 |
| 0·006893 | 0·88001 | 2·3218 | 141·4 | 0·004519 | 0·87804 | 2·3174 | 181·7 |
| 0·008248 | 0·88156 | 2·3316 | 140·2 | 0·006930 | 0·88009 | 2·3347 | 173·5 |
| 0·010161 | 0·88304 | 2·3445 | 139·9 | 0·01023 | 0·88298 | 2·3628 | 165·5 |
| 0·014641 | 0·88713 | 2·3759 | 139·1 | 0·011587 | 0·88430 | 2·3722 | 161·7 |
| $P_2 = 142·2$; $P_O = 97·4$; $\mu = 2·17$. | | | | $P_2 = 191·2$; $P_O = 146·4$; $\mu = 2·66$. | | | |

The author gratefully acknowledges his indebtedness to Mr. J. M. Skinner, who made the measurements of surface tension, and also to Dr. J. D. Loudon for assistance in the preparation of 2 : 3- and 2 : 4-dichloronitrobenzenes and for much helpful discussion.

UNIVERSITY OF GLASGOW. [*Received, March 31st*, 1944.]

---

## 110. *Steric Inhibition of Resonance. Part II. The* m-*Xylidines and* N-*Dimethyl*-m-*xylidines.*

By GEORGE THOMSON.

Corroboration of views expressed in Part I is given by the observation that the atomic refractivity of nitrogen in *N*-dimethyl-*m*-2-xylidine is lowered to nearly the value observed in aliphatic tertiary amines, whereas in *N*-dimethyl-*m*-5-xylidine it has the normal value for aromatic tertiary amines. An intermediate value is found in *N*-dimethyl-*m*-4-xylidine, in which one methyl group is ortho to the dimethylamino-group.

The molecular solution volume of *N*-dimethyl-*m*-2-xylidine is higher than that of *N*-dimethyl-*m*-5-xylidine but indistinguishable from that of *N*-dimethyl-*m*-4-xylidine.

The parachors of the *N*-dimethyl-*m*-xylidines decrease in the order *m*-5 > *m*-4 > *m*-2.

IN Part I (preceding paper) the view is expressed that inhibition of the resonance between a nitro-group and a benzene nucleus is accompanied by a lowering of molecular refractivity and that even a single bulky substituent ortho to a nitro-group will to some extent inhibit resonance. Since Hampson and his collaborators (J., 1937, 10; 1939, 981) have shown that steric inhibition of resonance by vicinal methyl groups is more marked in dimethylamino- than in amino-compounds, it becomes of interest to investigate the molecular refractivities of such compounds. Brühl (*Z. physikal. Chem.*, 1895, **16**, 497) noted that the atomic refractivity of nitrogen in *N*-dimethyl-*o*-toluidine was abnormally low, and this was confirmed by Ley and Pfeiffer (*Ber.*, 1921, **54**, 369), who found abnormalities in the absorption spectra and low molecular refractivities of ortho-substituted *N*-dimethylanilines and of *N*-dimethylxylidines in which methyl groups occupied one or both of the ortho-positions to the dimethylamino-group; when both ortho-positions were substituted the absorption spectrum was profoundly altered. On the other hand, no anomalies were found in the optical properties of ortho-substituted primary or secondary amines.

The present paper records a remeasurement of the molecular refractivities of *m*-4- and *m*-2-xylidines and their *N*-dimethyl derivatives, and measurements of the molecular refractivities of *m*-5- and *N*-dimethyl-*m*-5-xylidine and of the parachors of all six compounds, for it was desirable that these physical constants should be measured for all the compounds under the same conditions.

In Table I are recorded the values at 25° of densities, surface tensions (in dynes/cm.), and refractive indexes for five wave-lengths (mercury 4358 A. and 5461 A., hydrogen 4861 A. and 6563 A., and sodium 5893 A.). Table II contains the values of parachors and molecular refractivities calculated from the data of Table I together with some values from the literature, also the molecular solution volumes measured in benzene solution at 25°.

From Ley and Pfeiffer's measurements (*loc. cit.*) at 20° on *m*-2-xylidine and the *N*-dimethyl derivatives of *m*-2- and *m*-4-xylidines and those made by Brühl (*Z. physikal. Chem.*, 1895, **16**, 218) at 19·4° on *m*-4-xylidine, it would appear that *m*-2- has a higher density and higher refractive indexes than *m*-4-xylidine, whereas on

TABLE I.

| Substance. | $d_4^{25°}$. | $d_4^{100°}$. | $\gamma^{25°}$. | $\gamma^{100°}$. | $n_{4358}^{25°}$. | $n_{4861}^{25°}$. | $n_{5461}^{25°}$. | $n_D^{25°}$. | $n_{6563}^{25°}$. |
|---|---|---|---|---|---|---|---|---|---|
| Benzene | 0·87368 | — | — | — | 1·51979 | 1·50987 | 1·50210 | 1·49818 | 1·49340 |
| *m*-Xylene | 0·86010 | — | — | — | 1·5154 | 1·5061 | 1·4987 | 1·4949 | 1·4906 |
| Dimethylaniline | 0·95241 | — | — | — | 1·5900 | 1·5741 | 1·5621 | 1·5562 | 1·5496 |
| *m*-2-Xylidine | 0·97763 | — | 37·91 | — | 1·58662 | 1·57434 | 1·56369 | 1·55855 | 1·55273 |
| *m*-4-Xylidine * | 0·97185 | — | 36·49 | — | 1·5856 | 1·5725 | 1·5622 | 1·5570 | 1·5512 |
| *m*-5-Xylidine | 0·97038 | — | 36·38 | — | 1·58470 | 1·57150 | 1·56153 | 1·55635 | 1·55047 |
| Dimethyl-*m*-2-xylidine | 0·91507 | 0·8493 | 29·74 | 24·06 | 1·53552 | 1·52640 | 1·51762 | 1·51365 | 1·50920 |
| Dimethyl-*m*-4-xylidine | 0·91269 | 0·8474 | 30·88 | 24·15 | 1·54032 | 1·53070 | 1·52230 | 1·51808 | 1·51325 |
| Dimethyl-*m*-5-xylidine | 0·92751 | 0·8651 | 35·17 | 26·73 | 1·57272 | 1·55659 | 1·54772 | 1·54236 | 1·53631 |

* Buehler, Wood, Hull, and Erwin (*J. Amer. Chem. Soc.*, 1932, **54**, 2398) give $d^{25°}$ 0·9723, $\gamma^{25°}$ 36·75.

TABLE II.

| Substance. | $[P]^{25°}$. | $[P]^{100°}$. | $[R_L]_{4358}$. | $[R_L]_{4861}$. | $[R_L]_{5461}$. | $[R_L]_D$. | $[R_L]_{6563}$. | M.S.V. |
|---|---|---|---|---|---|---|---|---|
| Benzene | — | — | 27·14 | 26·64 | 26·36 | 26·17 | 25·97 | — |
| Dimethylaniline | — | — | 42·88 | 41·93 | 41·21 | 40·85 | 40·45 | — |
| *m*-Xylene | — | — | 37·19 | 36·62 | 36·17 | 35·93 | 35·67 | — |
| *m*-2-Xylidine | 307·1 | — | 41·57 | 40·86 (40·90) [1] | 40·24 | 39·94 (40·01) [1] | 39·59 (39·66) [1] | — |
| *m*-4-Xylidine | 306 [2] | — | 41·76 | 40·99 | 40·39 | 40·08 (40·04) [2] | 39·74 (39·68) [2] | — |
| *m*-5-Xylidine | 306·2 | — | 41·77 | 41·00 | 40·41 | 40·10 | 39·75 | — |
| Dimethyl-*m*-2-xylidine | 380·2 | 388·4 | 50·73 | 50·01 (49·96) [1] | 49·31 | 48·99 (49·01) [1] | 48·64 (48·65) [1] | 164·0 |
| Dimethyl-*m*-4-xylidine | 384·8 | 389·8 | 51·32 | 50·56 (50·49) [1] | 49·90 | 49·55 (49·48) [1] | 49·17 (49·13) [1] | 164·2 |
| Dimethyl-*m*-5-xylidine | 391·2 | 391·3 | 52·91 | 51·68 | 51·01 | 50·58 | 50·11 | 161·8 |

[1] Ley and Pfeiffer (*loc. cit.*). [2] Buehler, Wood, Hull, and Erwin (*loc. cit.*) give 307·2. [3] Brühl (*Z. physikal. Chem.*, 1895, **16**, 218).

dimethylation the position is reversed, *N*-dimethyl-*m*-2- having a lower density and lower refractive indexes than *N*-dimethyl-*m*-4-xylidine. The present density measurements agree with this conclusion in regard to *m*-2- and *m*-4-xylidine but not in regard to their dimethyl compounds. If we consider the difference of density between the xylidine and its *N*-dimethyl derivative we have the series *m*-5 < *m*-4 < *m*-2, *i.e.*, dimethylation of the vicinal xylidine results in the greatest lowering of density. The change in b. p. on dimethylation shows a similar regularity; whereas dimethylation *raises* the b. p. of aniline and of *m*-5-xylidine by 9° and 6°, respectively, it *lowers* the b. p. of *m*-4- and of *m*-2-xylidine by 9° and 22°, respectively. Such behaviour seems general: whenever a methyl group occupies a position ortho to the amino-group, dimethylation of the amine results in a lowering of b. p., whereas if the ortho-positions are unsubstituted a rise of b. p. results: *o*-toluidine (− 13°), *m*-toluidine (+ 8°), *p*-toluidine (+ 11°), *p*-xylidine (− 10°), *o*-xylidine (− 22°), mesidine (− 14°).

For each wave-length for which measurements have been made, the refractive indexes of the *m*-xylidines show only differences in the third decimal figure between the isomers, but they increase in the order *m*-5 < *m*-4 < *m*-2. On dimethylation the differences become greater (now affecting the second decimal figure); the order is reversed and becomes *m*-5 > *m*-4 > *m*-2. The molecular refractivities of *m*-5- and *m*-4-xylidines are indistinguishable; the value for *m*-2-xylidine is a little lower. The values for the dimethylxylidines are best discussed by reference to Table III, from which it is evident that the molecular refractivity of dimethyl-*m*-5-xylidine is normal as compared with dimethylaniline and dimethyl-*m*- and -*p*-toluidines, that whenever methyl or chlorine is substituted ortho to the dimethylamino-group it results in a reduction of approximately 1 c.c. in molecular refractivity, and that when both ortho-positions are occupied by methyl groups the molecular refractivity is lowered by about 1·6 c.c.

TABLE III.

| | $[R_L]_D$. | Δ. | | $[R_L]_D$. | Δ. |
|---|---|---|---|---|---|
| Dimethylaniline | 40·85 | 14·68 | Dimethyl-*p*-toluidine [1] | 45·68 | 14·62 |
| Benzene | 26·17 | | Toluene [2] | 31·06 | |
| Dimethyl-*m*-5-xylidine | 50·58 | 14·65 | Dimethyl-*m*-toluidine [1] | 45·68 | 14·62 |
| *m*-Xylene | 35·93 | | Toluene [2] | 31·06 | |
| Dimethyl-*m*-4-xylidine | 49·55 | 13·62 | Dimethyl-*o*-toluidine [1] | 44·62 | 13·56 |
| *m*-Xylene | 35·93 | | Toluene [2] | 31·06 | |
| Dimethyl-*m*-2-xylidine | 48·99 | 13·06 | Dimethyl-*o*-chloroaniline [1] | 44·95 | 13·57 |
| *m*-Xylene | 35·93 | | Chlorobenzene [2] | 31·38 | |

[1] Ley and Pfeiffer (*loc. cit.*). [2] Landolt–Börnstein, "Tabellen."

By calculation from Brühl's values of atomic refractivities the introduction of a dimethylamino-group into a hydrocarbon should result in a change of molecular refractivity in the aromatic series of 14·62 c.c., in the aliphatic series of 13·25 c.c.; from Eisenlohr's figures the value in the aliphatic series should be 12·78 c.c. The atomic refractivity of nitrogen in dimethyl-*m*-2-xylidine must therefore approach very closely the value for nitrogen in a tertiary aliphatic amine. Hampson's dipole-moment measurements (J., 1939, 981) have

indicated the almost complete suppression of the resonance of the dimethylamino-group by the vicinal methyl groups in dimethylmesidine and nitrodimethylaminodurene; the value 54·2 c.c. given by him for the molecular refractivity (λ 5461) of dimethylmesidine is in complete agreement with the results now recorded, for the difference between that value and the value of 41·06 c.c. for mesitylene (Part I) is 13·14 c.c., as compared with 14·85 c.c. for the difference between the molecular refractivities (λ 5461) of dimethylaniline and benzene and 13·14 c.c. for the difference between dimethyl-*m*-2-xylidine and *m*-xylene for the same wave-length. It is noteworthy that exaltation of molecular refractivity appears to be shown by *p*- (Marsden and Sutton, J., 1936, 599) and by *o*-nitrodimethylaniline (Ley and Pfeiffer, *loc. cit.*): it is well known that in *p*-nitrodimethylaniline, *p*-nitroaniline, and *o*-nitroaniline reinforcement of resonance effects leads to increased dipole moments.

There is an increase in molecular solution volume on passing from *N*-dimethyl-*m*-5- to *N*-dimethyl-*m*-4-xylidine, but the value for the latter is indistinguishable from that for *N*-dimethyl-*m*-2-xylidine. The values of molecular solution volume are practically identical with the values of $M/d$ for the pure liquids at the same temperature.

The parachors of the three *m*-xylidines are practically identical (306—307) but considerably lower than the sum of the atomic parachors (314·6); this low value is confirmed by Buehler, Wood, Hull, and Erwin (*loc. cit.*), who found the parachor of *m*-4-xylidine to be 307·2. For the *N*-dimethyl-*m*-xylidines the sum of the atomic parachors is 392·7: *N*-dimethyl-*m*-5-xylidine (391·2) is practically normal, but the parachors of the three isomers decrease in the order *m*-5 > *m*-4 > *m*-2 (a sequence confirmed by measurements at 100°), thus reversing the sequence found in the dichloronitrobenzenes (cf. Part I). This contrasting behaviour raises the question of the physical conception of the parachor. Interpretation of it as a molecular volume has been adversely criticised by Ferguson (*Nature*, 1930, **125**, 597) and by Reilly and Rae ("Physico-chemical Methods," 3rd edn., 1940, vol. 1, p. 110), the latter contending that it cannot have the dimensions of volume since it is calculated by multiplying $M/d$ (which has the dimensions of volume) by the fourth root of the surface tension (which is not dimensionless) measured at the same temperature as $d$. Now the molecular refractivity has undoubtedly the dimensions of volume: it is again $M/d$ multiplied by a factor [in this case $(n^2 - 1)/(n^2 + 2)$], and the molecular solution volume when measured in benzene solution approximates closely to the value of $M/d$ for the pure liquid at the same temperature; since the data for the dichloronitrobenzenes (cf. Part I) and the data now presented show that in a series of position isomers, although the molecular solution volume may increase, the molecular refractivity can decrease, there seems to be no reason why in such homologous series variations in the parachor should of necessity have always the same sign as variations in either of these other properties.

## Experimental.

Refractive indexes were measured on a Hilger–Pulfrich refractometer, and surface tensions at 25° by Sugden's differential bubble-pressure method and at 100° by Ferguson's method (cf. Part I). In calculating the parachors the density of the saturated vapour has been neglected.

*Materials.*—*m*-Xylene, dimethylaniline, *m*-4- and *m*-2-xylidine were obtained by repeated fractionation of products supplied as these specific compounds by B.D.H. The b. p.'s of the fractions used were: *m*-xylene 139°, dimethylaniline 192·5°, *m*-4-xylidine 213·5—214°, *m*-2-xylidine 216·5—217°. The molecular refractivities are in good agreement with those recorded in the literature. *m*-5-Xylidine was prepared from *m*-4-xylidine by Haller and Adams's method (*J. Amer. Chem. Soc.*, 1920, **42**, 1840) and purified by crystallisation of the acetyl derivative. The fraction used boiled at 223°/774 mm.

The dimethylxylidines were prepared by methylation with methyl sulphate. Use of acetic anhydride to remove unchanged or monomethylated amine was unsatisfactory (since the *N*-acetomethyl-*m*-2- and -*m*-4-xylidides have b. p.'s very close to those of the *N*-dimethylxylidines), and in the methylation of *m*-2-xylidine it was replaced by *p*-toluenesulphonyl chloride. The *N*-dimethyl-*m*-2-xylidine had b. p. 194·5—195°/760 mm. (Found: C, 80·3; H, 9·9. Calc. for $C_{10}H_{15}N$: C, 80·5; H, 10·1%). For methylation of *m*-4- and *m*-5-xylidines the method of Evans and Williams (J., 1939, 1199) was adopted. *N*-Dimethyl-*m*-4-xylidine had b. p. 204·5—205°/747 mm. (Found: C, 80·3; H, 9·9%). *N*-Dimethyl-*m*-5-xylidine had b. p. 228·5—229°/772 mm. (Found: C, 80·8; H, 10·1%); picrate, m. p. 192° (Found: C, 50·9; H, 4·5. Calc. for $C_{16}H_{18}O_7N_4$: C, 50·8; H, 4·8%).

Reference has been made to the surprising similarity in b. p. of *N*-dimethyl- and *N*-acetylmethyl-xylidines. *N*-Acetomethyl-*m*-4-xylidide (Found: C, 74·5; H, 8·9. Calc. for $C_{11}H_{15}ON$: C, 74·6; H, 8·5%) boils at 205—205·5°/747 mm., only 0·5° higher than *N*-dimethyl-*m*-4-xylidine. The refractive indexes are also practically identical, but the densities differ considerably. Physical constants measured are as follows:

| | $d_{4°}^{14·3°}$. | $d_{4°}^{20·6°}$. | $d_{4°}^{21·1°}$. | $d_{4°}^{23°}$. | $n_{5461}^{25°}$. | $n_{5893}^{25°}$. | $n_{6563}^{25°}$. |
|---|---|---|---|---|---|---|---|
| *N*-Dimethyl-*m*-4-xylidine | 0·92124 | 0·91621 | — | 0·91269 | 1·52230 | 1·51809 | 1·51325 |
| *N*-Acetomethyl-*m*-4-xylidide | 0·92672 | — | 0·92023 | 0·91696 | 1·52239 | 1·51817 | 1·51334 |

*Molecular solution volumes in benzene solution.*

| | $f_2$. | $d_{4°}^{25°}$. | M.S.V. | $f_2$. | $d_{4°}^{25°}$. | M.S.V. |
|---|---|---|---|---|---|---|
| (Benzene) | — | 0·87342 | — | — | — | — |
| *N*-Dimethyl-*m*-5-xylidine | 0·082768 | 0·88013 | 161·8 | 0·097186 | 0·88114 | 161·8 |
| *N*-Dimethyl-*m*-4-xylidine | 0·08647 | 0·87838 | 164·3 | 0·13041 | 0·88077 | 164·2 |
| *N*-Dimethyl-*m*-2-xylidine | 0·087024 | 0·87863 | 164·1 | 0·13002 | 0·88107 | 163·9 |

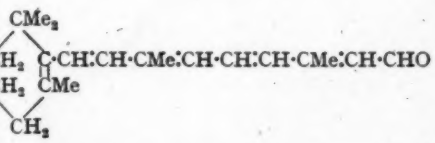
The author is indebted to Mr. James R. Sim and Mr. Victor C. Farmer for assistance with the experimental work, and to Mr. J. M. Cameron for the micro-analyses.

University of Glasgow. [*Received, March 31st*, 1944.]

# NOTE.

*Vitamin-A Aldehyde (Axerophthal).* By E. G. E. HAWKINS and R. F. HUNTER.

PREVIOUS attempts to prepare vitamin-A aldehyde (axerophthal) by Oppenauer oxidation of vitamin-A alcohol in the presence of acetone (Batty, Burawoy, Harper, Heilbron, and Jones, J., 1938, 175) and diethyl ketone (Haworth, Heilbron, Jones, Morrison, and Polya, J., 1939, 128) led to the formation of axerophthylideneacetone and a $C_{22}$ aldehyde whose ultra-violet absorption spectrum indicated that it contained a conjugated double bond more than vitamin-A aldehyde. The aldehyde has now been prepared by oxidation of vitamin-A alcohol with aluminium *iso*propoxide in the presence of acetaldehyde.



On Pondorff reduction, the aldehyde regenerated vitamin-A alcohol and on condensation with acetone in the presence of sodium ethoxide it furnished axerophthylideneacetone.

Ultra-violet spectroscopic measurements were made in purified *cyclo*hexane.

(i) A mixture of a distilled vitamin-A alcohol concentrate prepared from the unsaponifiable matter of whale liver oil ($E^{1\%}_{1\,cm.}$ = 1230 at 3250 A.) (1·2 g.), aluminium *iso*propoxide (2 g.), acetaldehyde (15 c.c.), and benzene (40 c.c.) was heated in a sealed tube at 70° for 48 hours. The product was treated with water and extracted with benzene, and the filtered extract dried with sodium sulphate and evaporated under reduced hydrogen pressure. The residue was dissolved in *cyclo*hexane (20 c.c.) and a portion of the solution was chromatographed on weakened "Mayfair" alumina under slight nitrogen pressure (cf. Hunter and Scott, *Biochem. J.*, 1941, **35**, 31). Elution of the main yellow zone furnished material which showed bands at 3680 and 3500 A., with a slight inflection at 3300 A. in the ultra-violet and maxima at 6580 and 6200 A. in the antimony trichloride reaction, indicating the presence of a small amount of unchanged vitamin-A alcohol. On treatment with alcoholic hydrogen chloride under the usual conditions (Hawkins and Hunter, *Biochem. J.*, 1944, **38**, 34) and further chromatography, however, a product was obtained which showed only a single band at 6570 A. in the antimony trichloride reaction. This material showed bands at 3650 and 3480 A. in the ultra-violet.

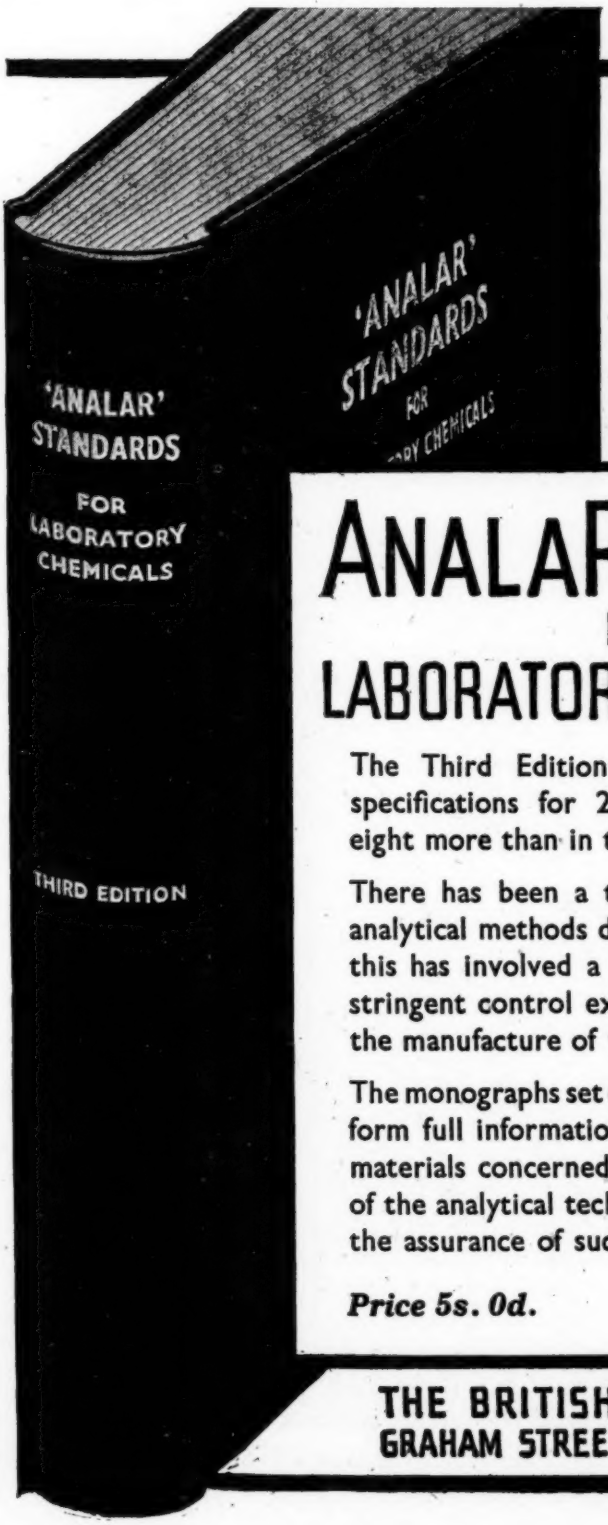
(ii) A further quantity of vitamin-A aldehyde was prepared in a similar manner from a chromatographed distilled concentrate of vitamin-A alcohol and was freed from unchanged vitamin-A alcohol by "cyclisation" and chromatography. This showed bands at 3680 and 3500 A. in the ultra-violet ($E^{1\%}_{1\,cm.}$ = 1050 at 3680 A. and 920 at 3500 A.) and a maximum at 6570 A. ($E^{1\%}_{1\,cm.}$ = 2900) in the antimony trichloride reaction. The *dinitrophenylhydrazone*, prepared by heating with 2 : 4-dinitrophenylhydrazine in aqueous alcohol containing a small amount of hydrochloric acid in an atmosphere of hydrogen at 60° for 15 minutes, separated from acetone in brownish-black crystals, m. p. 208—209° (Found: C, 67·0, 66·9; H, 7·0, 7·1. $C_{26}H_{32}O_4N_4$ requires C, 67·25; H, 6·9%). This showed an absorption band at 4350 A. ($E^{1\%}_{1\,cm.}$ = 1060).

On Pondorff reduction with aluminium *iso*propoxide, vitamin-A aldehyde regenerated vitamin-A alcohol, which showed absorption maxima at 3300 A. and at 6200 A. in the ultra-violet and the antimony trichloride reaction respectively. This was characterised by conversion into "cyclised" vitamin-A, which showed absorption bands at 3900, 3700, and 3500 A. in the ultra-violet and a maximum at 6200 A. in the antimony trichloride reaction.

The aldehyde underwent fairly rapid oxidation on keeping in solution at 0°, yielding material which on chromatography on alumina furnished a main yellow zone containing a compound which showed a band at 3300 A. in the ultra-violet and at 6180—6200 A. in the antimony trichloride reaction. This differed from vitamin-A alcohol in that the ultra-violet absorption spectrum was unaltered after treatment with alcoholic hydrogen chloride in the usual way.

*Synthesis of Axerophthylideneacetone from Vitamin-A Aldehyde.*—A solution of vitamin-A aldehyde in acetone was cooled to −5°, treated with alcoholic sodium ethoxide, kept at laboratory temperature, with occasional shaking, for 2½ hours, and then extracted with benzene–light petroleum. The extract was washed in turn with dilute phosphoric acid, aqueous sodium carbonate, and water, and evaporated under reduced hydrogen pressure. The product showed main absorption bands at 3950 and 7320 A. in the ultra-violet and the antimony trichloride reaction respectively, characteristic of axerophthylideneacetone (Hawkins and Hunter, *loc. cit.*), which were not substantially altered by chromatography. On reduction with aluminium *iso*propoxide, the condensation product furnished axerophthylidene*iso*propyl alcohol which showed absorption bands at 3500 and 7130—7150 A. in the ultra-violet and the antimony trichloride reaction respectively (cf. Heilbron, Johnson, and Jones, J., 1939, 1563).

We thank the Directors of Lever Brothers and Unilever Ltd. for permission to publish these results.—CENTRAL TECHNICAL DEPARTMENT, LEVER BROTHERS & UNILEVER LIMITED, PORT SUNLIGHT. [*Received, April 24th*, 1944.]




*Third Edition now ready*

# ANALAR STANDARDS FOR LABORATORY CHEMICALS

The Third Edition of this book contains specifications for 228 'AnalaR' chemicals: eight more than in the First Edition.

There has been a thorough revision of the analytical methods described in the book, and this has involved a further tightening of the stringent control exercised over all stages in the manufacture of 'AnalaR' chemicals.

The monographs set out in the clearest possible form full information as to the purity of the materials concerned, as well as a description of the analytical technique by means of which the assurance of such purity is established.

***Price 5s. 0d.*** ***postage extra***

**THE BRITISH DRUG HOUSES LTD**
**GRAHAM STREET LONDON N.1**

# For TEXTILE DYEING

Hank Dyeing Machine by Longclose Engineering Co. Ltd., Leeds, 10.

**FIRTH-VICKERS STAINLESS STEELS LTD SHEFFIELD**


PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD., BUNGAY, SUFFOLK.